Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product

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Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product

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by

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SUMMARY

Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product

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Orange waste was first saponified with $Ca(OH)_2$ and then loaded separately with La(III), Ce(III) and Zr(IV) ions to investigate feasible adsorption of arsenic as well as phosphate from aquatic environment. The metal loaded gels were found to be efficient for arsenate and phosphate adsorption at neutral pH while adsorption of arsenite was found to happen at pH 9~10. Among all three gels, Zr(IV)-loaded SOW gel was proved to be the best because of its high adsorption capacity. The Zr(IV)-loaded SOW gel was found to be superior to commercial resins (zirconium ferrite and MUROMAC XMC 3614) in case of phosphate adsorption. However, adsorption of arsenic and phosphate was deemed to follow pseudo-second-order kinetics. Presence of common competing anions e.g. chloride, carbonate, sulfate did not interfere the adsorption of arsenate but phosphate did interfere so much. In addition, chloride, carbonate, sulfate and arsenate did not interfere the adsorption of phosphate on the Zr(IV)-loaded SOW gel. Both La(III)- and Zr(IV)-loaded SOW gels were tested for continuous-mode adsorption at laboratory scale by using a column set up. After complete saturation of the column, quantitative elution was also found to occur with either sodium hydroxide or hydrochloric acid. The loaded La(III) was found to be eluted during elution tests but Zr(IV) was not eluted in the tested condition. This signifies that the immobilization with Zr(IV) gives a superior gel for adsorption and recovery purposes. The excellent anion sequestering capability of the gels, which have been originated from an agricultural by-product (orange waste), would lead to the development of cost-effective adsorbents for arsenic and phosphate removal from aquatic environment.

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Chapter 1

General Introduction

1.1. THESIS RATIONALE

With the demonstrated advantages of adsorption process over other conventional techniques is nowadays of greatest importance. Application of adsorbents for removal of arsenic, phosphate and other hazardous materials has drawn attention due to higher sorption capacity and repetitive use of the material. Among those adsorbents the agricultural by-products and/or bio-materials have got utmost importance because of their low cost, availability and reasonably high adsorption capacities. Apart from that, the commercial viability of such adsorbents is becoming more and more likely. A wide range of agricultural by-products and bio-materials have so far been studied in the view of getting efficient and cost effective adsorbents. Hitherto rice husk, sea weeds, bio-char, fungal biomass, chicken feathers, yeast biomass, algae and so forth have been studied by the researchers considering their prospect to be converted as adsorbents. Orange waste is such an agricultural by-product generated in the juicing factories, which can be modified to convert into a suitable adsorbent for the removal of hazardous anions due to excess charge of metal ion complexed with the carboxylic acid contents in it. The usage of chemically modified orange waste in phosphate and arsenic adsorption is relatively new and hence this study represents a novel work in this field.

On the other hand, in working towards a sustainable society, recycling and recovery of essential elements with handling of scarce resources must be considered. The growing quantities of sludge from wastewater treatment plants and the increasingly stringent restrictions on landfilling and on agricultural use of sludge are promoting other disposal alternatives. Sludge fractionation, product recovery and separation of toxic and/or important elements have gained particular interest. A part of this whole thesis has been dealt with the potential for phosphate release and recovery from incinerated activated sludge ash (IASA), a phosphate-rich residue. Considering the

growing concern of global exhaustion of phosphorus, a limiting nutrient, the work is thought to be highly cherished.

1.2. AIMS AND OBJECTIVES

One of the objectives of this work was to remove arsenic species applying adsorption technique from aquatic environment by using a low-cost and available agricultural by-product, orange waste. This precursor was chemically modified in the laboratory in a simpler way and used as an adsorbent for the removal of hazardous anions. Keeping this in mind, the operating conditions were optimized by conducting a numbers of experiments from various points of view. Effect of pH on arsenic adsorption was tested to find out operating pH range, effect of presence of other competing anions was tested to find its influence on arsenic adsorption, and column tests were carried out to find the effectiveness of this adsorbent in continuous operation, which is more practical and industry-oriented.

On getting a quite satisfactory outcome of arsenic removal, the work was extended onwards and further modification of the adsorbent was done to find its applicability for phosphate adsorption from the aqueous solution. Splendid results, from the viewpoint of adsorption capacity, were obtained. Various parameters such as pH, temperature, concentration etc. were applied to get an optimum operating condition. Kinetic studies, effect of other anions, applicability to real waste water were tested and analyzed and results were published in international scientific forums.

Finally the work was driven through to the extraction of phosphorus from IASA by acidification followed by recovery of this element from the leachate by using orange waste gel. Acid extraction was employed because it has been established to be an effective as well as simple method for extraction. This research gives an idea for the recovery of invaluable element, phosphorus, from IASA.

1.3. SUMMARY AND OUTLINE OF THE THESIS

Although numerous studies have been appeared in the field of arsenic and phosphate removal using various techniques, less attention has been paid on the application of agricultural by-products for this purpose. However, this dissertation is the outcome of a study, which was carried out to gain more scientific and practical

insights into the removal and recovery of arsenic and phosphorus from aqueous medium and to develop an optimum operating condition for this. The work has also been extended to understand the extraction behavior of phosphorus from IASA and to recover that extracted elements, phosphorus in particular, by using the prepared adsorption gel.

The thesis was subdivided into two different parts depending on the objective of works. Part-I describes the removal and recovery of arsenic from aqueous solution, while Part-II explains that of phosphate from synthetic solution as well as real solution. The application of the prepared gel has been incorporated in Part-II as well, where industrial solution has been treated with the Zr(IV)-loaded saponified orange waste (SOW) gel and in addition phosphate recovery from IASA has also been described. Both parts contain introduction, research background and literature review, experimental methods, results and discussion, and conclusion. The overall conclusion of the work and future directives for further works are presented in Chapter 12.

A list of publications resulting from these works is given in Appendix A. In Appendix B a list of contributions to scientific forum is placed whereas Appendix C provides curriculum vitae of the author.

Part I

Adsorptive removal of arsenic from aqueous solution by using metal-loaded saponified orange waste gels

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Chapter 2

Introduction

2.1. INTRODUCTION

Arsenic (atomic number 33) is a member of the Nitrogen family with both metallic and non-metallic properties, and is a naturally occurring element in the earth's crust, air, and all living matters [1]. It is a toxic element, which is known to be a risk to aquatic flora and fauna and human health even in relatively low concentration. It is a ubiquitous element that ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in seawater and 12th in human body [2]. The name "arsenic" is derived from the Greek word *arsenikon*, which means potent. Arsenic is present in more than 200 mineral species and is widely distributed in the environment; especially as arsenopyrite or as metal arsenates [3]. It has been estimated that about one third of the atmospheric flux of arsenic is on natural origin. It is introduced into water through natural sources [3] e.g. volcanic emissions, dissolution of mineral ores, atmospheric deposition etc. as well as through anthropogenic sources [4,5] e.g. non-ferrous smelting, petroleum-refining, fossil fuel power plants and the use of arsenical pesticides and herbicides. Even though the use of arsenic-containing products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common [6]. The impact of the environment of the use of arsenical compounds, at least locally, will remain for some years.

Arsenic occurs in two primary forms: organic and inorganic. Organic species of arsenic are predominantly found in foodstuffs and marine organisms, such as shellfish in the form of monomethyl arsenic acid, dimethyl arsenic acid, arseno-sugars, arsenobetaine. Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important [7]. However, arsenic occurs in environment in different oxidation states (-3, 0, +3 and +5). In oxidized environment arsenic appears mostly as oxyanions [8]. Arsenic cannot be easily destroyed and can only be converted into different forms or transformed into insoluble

compounds in combination with other elements, such as iron. Many impurities such as lead, iron and selenium may be mixed up together with arsenic wastes and make it uneconomic to remove.

It has been well-established that arsenic compounds have detrimental effects on health of living beings. Incidents of arsenic contamination in groundwater have been reported from all over the world [9]. Chronic exposure to arsenic concentrations above 100 µg/l can cause vascular disorders, such as dermal pigments (Blackfoot disease) and skin, liver and lung cancer [10,11]. Naturally occurring arsenic, however, is of great concern in some regions of Bangladesh, India and Nepal, where hazardous concentrations of arsenic have appeared as a result of strong water-rock interactions and the physical and geochemical conditions for arsenic mobilization in aquifers [7]. Of various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health and high arsenic concentrations can be found in groundwater. In water it is commonly found in inorganic species such as arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As(III) and As(V), respectively [12], which have harmful effects on humans, plants and animals as well. In 1993, based on human health data the World Health Organization (WHO) has recommended a maximum contaminant level for arsenic (10 µg/l) in drinking water but many countries have retained the earlier WHO guideline of 50 µg/l including Bangladesh, India and China [13]. Therefore processes to remove excess arsenic from drinking water are urgently required.

2.2. CONVENTIONAL ARSENIC REMOVAL METHODS

There are numbers of arsenic removal methods, which include coagulation followed by precipitation, lime softening, membrane separation, ion exchange, adsorption etc.

2.2.1. Coagulation-filtration

The most heavily documented treatment methods for arsenic removal involve coagulation and filtration, either using metal salts or lime softening. Apart from arsenic removal, this treatment can effectively remove many suspended and dissolved constituents from water: turbidity, iron, manganese, phosphate and fluoride are few to

mention. Thus coagulation and filtration to remove arsenic will improve other water quality parameters, resulting in ancillary health and aesthetic benefits. In this technology removal is highly dependent upon initial arsenic concentration, dosage of coagulant, pH and the valence of the arsenic species. During coagulation and filtration, arsenic is removed through three main mechanisms [14]:

- Precipitation: the formation of insoluble compounds e.g. $Al(AsO_4)$ or $Fe(AsO_4)$
- Coprecipitaion: the incorporation of soluble arsenic species into a growing metal hydroxide phase
- Adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role [15]. Ferric ion coprecipitation is particularly useful in the mining industry, where large amounts of ferric ion and arsenic can be by-products of production or refining. Of all the coagulants studied, ferric chloride and ferric sulfate have been most successful. Ferric ion coprecipitation of arsenite is moderately effective with 50% removal at a pH of 7.0 [16]. The use of iron hydroxides for the co-precipitation of arsenic in industrial wastewater (in which arsenic is in the mg/l range) requires iron dosage 4 to 8 times higher than that of the soluble arsenic, a greater iron dosage yields no further benefit [17]. Suspended aluminum salts (alum) can remove arsenate via mechanisms similar to those for ferric hydroxides. However, it is less effective over a narrower pH range for arsenate removal and is ineffective for removal of arsenite [18]. The highest overall removal (99.9%) was achieved with addition of 40 mg/l ferric sulfate at pH 7.5 [19]. However, a problem with this technique is the safe separation, filtration, and the handling and disposal of the contaminated coagulant sludge. Moreover, in many instances it seems to be difficult to lower the arsenic concentration to the acceptable level by this technique.

2.2.2. Physical removal

Some synthetic membranes are permeable to certain dissolved compounds but exclude others. Because of their selective permeability for different compounds, such

membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds. High pressures are required to cause water to pass across the membrane from a concentrated to dilute solution. For this reason membrane separation is addressed as a pressure driven process. Generally such processes are divided into four categories, which are microfiltration (pore size of 0.05-10 μm), ultrafiltration (pore size of 0.002-0.1 μm), nanofiltration (pore size of 0.001-0.003 μm) and hyperfiltration or reverse osmosis (pore size<0.001 μm). Separation is accomplished by microfiltration and ultrafiltration membranes via mechanical sieving while capillary flow or solution diffusion is responsible for separation in nanofiltration and reverse osmosis membranes. Lately advancement of membrane technology has taken place in the name of electro-ultrafiltration [20], which is found to possess good potential in treating arsenic from water.

2.2.2.1. Microfiltration

Han et al. [21] studied the feasibility of combination of flocculation and microfiltration for arsenic removal from drinking water and concluded that with the addition of a small amount of cationic polymeric flocculant can greatly increase the permeate flux during microfiltration. Shih [22] had showed an overview of arsenic removal on pressure driven membrane process and explored the parameters that may influence the arsenic removal efficiency by membrane technologies such as source water parameters, membrane material, membrane types and membrane process.

2.2.2.2. Ultrafiltration

Separation is reported to be accomplished by ultrafiltration membrane via mechanical sieving [23]. This separation technology is more effective at low pressure operation than the other membrane technologies. Legault et al. [24] studied arsenic removal from water by using ultrafiltration and demonstrated a high degree of arsenic removal. Retention of arsenic was reported to depend on the presence of the background salt at different concentration. Brandhuber and Amy [25] explored the possible influence of natural organic matter on As(V) rejection by charged ultrafiltration membranes.

2.2.2.3. Nanofiltration

Nanofiltration is considered as one of the methods that can be used to meet regulations for lowered arsenic concentrations in drinking water. Waypa et al. [26] studied removal of arsenic from synthetic freshwater and from surface water by nanofiltration as well as reverse osmosis process and reported that both membranes can achieve rejections of 99% over a range of operational conditions. Urase et al. [27] studied the effect of pH on the rejection change and showed that electrically charged membranes generally have a higher rejection for charged solutes than for non-charged solutes. Saitúa et al. [28] reported that arsenic rejection was independent of transmembrane pressure, cross flow velocity and temperature. Over 95% of arsenate and 75% of arsenite removal was found without any influence of chemical compositions of source water [29].

2.2.2.4. Reverse osmosis

Reverse osmosis membranes have also been known as another alternative to remove arsenic in water. Kang et al. [30] found that the removal of As(V) is much higher than As(III) over a pH range of 3-10. Ning [31] had reviewed the removal of arsenic by reverse osmosis and concluded that As(V) is very effectively removed while As(III) removal is also possible by this process at sufficiently high pH.

The membrane technologies, as a whole, are very little used when the objective is to remove only the arsenic and when this element is the only one contaminant in the raw water. The drawbacks of using of membrane technology in arsenic removal have been reviewed as follows [32]:

- The systems are more costly than other treatment methods.
- The discharge of the concentrate can be a problem.
- Water loss associated with concentrate stream poses a problem.
- Membrane fouling may occur.

The use of such membranes are justified when the total dissolved solids due to the presence of sulphates, nitrates, carbonates etc. are important and required to be treated. In practice, the in-line coagulation used before a membrane treatment (microfiltration or ultrafiltration) provides very good performances [33]. Several issues, however, still remain to be resolved which include membrane reversible fouling, chemical cleaning

frequency, the optimum cost and benefits of chemical pre-treatment to microfiltration and ultrafiltration membrane systems [34].

2.2.3. Ion exchange

Ion exchange is a physical/chemical process in which ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge in a solution. It is a reversible interchange where there is no permanent change in the structure of the solid. The solid is typically a synthetic anion exchange resin, which is used to remove particular contaminants of concern. Ion exchange is commonly used in drinking water treatment for softening (i.e. removal of calcium, magnesium etc. in exchange of sodium) as well as removing nitrate, arsenate, selenate etc. from municipal water [35]. Ion exchangers are typically down-flow, packed bed columns with ion exchange resin beads pre-saturated with an exchangeable ion. Source water is passed through the packed bed until the appearance of the unwanted contaminant in the effluent. Generally, contaminated-water is passed through one or more ion exchange resin beds. Arsenate and several other anions are preferentially removed according to the order of preference for exchange. After continuous operation for a certain time all available sites on the resin have been exhausted due to the adsorption of target elements. At this stage, the ion exchange media have to be reactivated with a regenerant solution and rinsed with water in preparation for another treatment cycle.

Ion exchange does not remove As(III) because As(III) occurs predominantly as a neutral species in water with pH value less than 9 [35]. The predominant species of As(V) are negatively charged, and thus are removed by ion exchange. Anion exchange resins are prone to chromatographic due to the presence of competing anions in the treated water. Consequently, the efficiency of the ion exchange process for arsenic removal is strongly affected by competing ions. Other factors affecting the use of the ion exchange process include contact time and spent regenerant disposal. The level of competing anions often determines the applicability of ion exchange process. The following selectivity sequence was reported for strong-base anion resin [35].

$$SO_4^{2-} > NO_3^- > HAsO_4^{2-} > NO_2^-, Cl^- > H_2AsO_4^-, HCO_3^- > H_3AsO_4$$

Due to its higher treatment cost compared to conventional treatment technologies, ion exchange application is limited primarily to small-to-medium-scale. However, sulfate, selenium, fluoride, and nitrate compete with arsenic and can affect the removal process. So the low selectivity in the presence of other competing anions [36] has made this process less attractive. In spite of everything, ion exchange is an area of intense research where the development of anionic chelating exchange resins or ion exchange polymers may dramatically improve the technology for arsenic treatment.

2.2.4. Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid or gas/solid boundary layer. It is a mass transfer process, which involves separation of a substance from one phase accompanied by its accumulation at the surface of another. This process, employing solids such as activated carbon, metal hydrides and synthetic resins, is used widely in industrial applications for purification of water and wastewater. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface.

The use of carbon as an adsorbent extends far back into history. Charcoal was used for drinking water filtration by ancient Hindus in India [37]. With the course of time selective adsorption utilizing biological materials, mineral oxides, activated carbons or polymer resins has mounted enthusiasm. However, industrial production of modern activated carbon was established in the early 19^{th} century while the activated carbon was first reported for water treatment in the United States in 1930 [38]. Activated carbons have been prepared from a wide variety of sources such as sawdust, rice hulls, coconut shells, wood char, bone-char, petroleum coke and so forth. The surface chemistry of carbon generally depends upon the activation conditions applied where activation refines the pore structures. Surface area up to 2000 m^2/g has been reported to be obtained upon proper activation of carbon. High surface area, however, does not necessarily mean high adsorption capacity. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH etc. Many activated carbons are available but few are selective. These are expensive as well. Therefore the research thirst over the years is leading to find improved and tailor-made materials,

which will meet several requirements such as regeneration capability, easy availability, cost effectiveness etc. Consequently, low-cost adsorbents have drawn attention to many researchers and characteristics as well as application of many such adsorbents are reported. However, low-cost adsorbents are discussed herein after.

2.2.4.1. Low-cost adsorbents

Adsorption of arsenic using natural products and biomass has emerged as an option for developing economic and eco-friendly wastewater treatment processes. Numerous low-cost adsorbents have so far been studied for the removal of arsenic from water and wastewater. Red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides and various bioadsorbents are few to mention.

Red mud is a ferric hydroxide material, the by-product of smelting and refining of ores containing gold, cobalt, silver, copper and iron. It has been explored as an alternate adsorbent for arsenic. Arsenic adsorption on red mud is pH dependent and an acidic solution having pH range 1.1-3.2 favored As(V) removal while alkaline aqueous medium (pH ≈ 9.5) was effective for As(III) removal [39]. Heat and acid treated red mud has also been reported to have better adsorption capacity for arsenic removal [40].

Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. In the past, fly ash was generally released into the atmosphere via the smoke stack, but pollution control equipment mandated in recent decades. Presently it is required that the pollutant must be captured prior to the release of smoke. Since aluminosilicates are the major chemical compounds of fly ash, it has been tested for its adsorption capability. Removal of arsenate at pH 4 was reported higher than that at pH 7 or 10 by using fly ash collected from coal power stations [41].

Zeolites are basically hydrated alumino-silicates having micro-porous structure that can accommodate a wide variety of cations without any change in structure. It has been received increasing attention for pollution control in wastewater treatment. More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are so far known [42]. Adsorption of arsenate and aresenite on zeolites was studied along with activated carbon [43]. Approximately 50% removal of arsenate on zeolite was

reported while activated carbon removed nearly 60% of the same. Xu et al. [44] studied adsorption and removal of As(V) from drinking water by aluminum-loaded shirasu-zeolite and found its effectiveness over a wide range of pH (3-10). Common competing anions such as chloride, nitrate, sulfate etc. had little effect on As(V) adsorption but phosphate greatly interfered with the adsorption.

Numerous biological materials have been tested for removal of toxic ions from aqueous solutions over the last two decades. However, only a limited number of studies have investigated the use of bioadsorbents e.g., bio-char [12], methylated yeast biomass [45], fungal biomass [46], chicken feathers [47], alginate [48] to remove arsenic from aqueous solution. It is noteworthy that biological materials represent a potential source of abundant low-cost adsorbents and there is no environmental or technical reason which impedes the preparation of adsorbents by using those materials.

Biochar is a type of charcoal produced from biomass via pyrolysis. Due to its low cost and local availability, biochar has drawn attention in the wastewater treatment arena. Biochar, generated as a by-product from wood/bark pyrolysis, has been investigated for arsenic along with cadmium and lead [12]. Maximum adsorption of arsenic was reported to occur at pH 3-4.

Chitosan, one of the common bioadsorbents, is produced from chitin, which is the structural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish etc.). Chitin, a long-chain polysaccharide, is the most widely occurring natural carbohydrate polymer next to cellulose. Dambies et al [49] tested the adsorption of As(V) onto molybdate-impregnated chitosan gel bead and reported that the sorption capacity increased with the impregnation and optimum pH was 3. Powdered chitosan, obtained from shrimp shell, was converted into bead form [50] and used to remove arsenic from water in both batch and continuous process.

2.3. CHARACTERISTICS OF ORANGE WASTE

Crude orange waste was kindly donated by a local fruit juice industry, JA Saga Beverage Ltd., Japan. The large share of this waste is orange peels, while the remaining is the rag, comprising the fruit core and segment membranes after juice extraction. It is, however, estimated that approximately 20% of the weight of a whole

orange is peel, and about 10% of the weight of the fruit is segment membrane [51]. Orange waste consists of cellulose, hemicellulose, pectin, limonene and many other low molecular weight compounds. Table 2.1. shows the % distribution of various polysaccharide fractions [51] in orange from where it is obvious that an appreciable amount of pectin is present in orange waste. In this study orange waste was chosen to prepare adsorbent for its pectin content. Pectin is a carboxylated polysaccharide in which pectic acid is partly esterified by a methyl group [52]. It can be easily converted into pectic acid by saponification with alkalis and can be loaded with metal to make adsorption gel [53].

Table 2.1. Percentage (%) distribution of various polysaccharide fractions in different component parts of orange.

	Pectic substance	Cellulose	Hemicellulose	Others
Peel	55.4	31.2	8.7	4.9
Pulp	68.0	25.1	6.8	0.1
Juice	88.7	--	11.3	0

2.4. RESEARCH OBJECTIVES

The present study has dealt with the preparation of adsorption gel using orange waste precursor and the investigation to obtain a deeper understanding about arsenic adsorption onto the prepared gel. Attention has also been given to determine adsorption mechanism and kinetics. However, the main objectives of this study are summarized as follows:

- To produce orange waste gel in the view of removal of arsenic from aquatic medium.
- To investigate the role of metal-loaded orange waste gel for its adsorption behavior.
- To determine the maximum adsorption capacity of the gel for arsenic removal.
- To study the kinetic behavior, pH dependence, effect of the presence of foreign anions and to analyze the data.
- To contribute to the protection of environment and improve human health.

Chapter 3

Research Background and Literature Review

3.1. OCCURRENCE OF ARSENIC IN THE ENVIRONMENT

Arsenic, a common element in nature, is a naturally occurring contaminant of drinking water and can be found in the earth's crust, ground and marine water and in the organic world as well. It is found in groundwater as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favorable for arsenic accumulation. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions [7] as well as through a range of anthropogenic activities such as gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants and the use of arsenical pesticides and herbicides [4,5]. Nriagu and Pacyna [54] estimated that anthropogenic sources of atmospheric arsenic amounted to be around 18,800 ton per annum, which is approximately 70% of the global atmospheric arsenic flux. Arsenic occurs in two primary forms such as organic and inorganic. Organic species, predominantly found in foodstuffs e.g. shellfish, are produced mostly in surface waters by biological activity but are rarely quantitatively important [7]. Inorganic arsenic, on the other hand, occurs in two valence states, arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), which are commonly referred to as As(III) and As(V), respectively [12].

3.2. SOURCES OF ARSENIC

Arsenic occurs as a major constituent in more than 200 minerals (ore minerals or their alteration products), which include elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenite. The most abundant arsenic ore minerals are arsenopyrite (FeAsS) and arsenian pyrite ($Fe(S,As)_2$). It is generally believed that arsenopyrite, together with the other dominant sulphide minerals (realgar and orpiment) are only formed under high temperature conditions in the earth's crust [7].

Though not a major component, arsenic is also often present in varying concentrations in other common rock-forming minerals. Since the chemistry of arsenic follows closely that of S, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Arsenic may also present in the crystal structure of many other sulphide minerals as a substitute for sulfur. Arsenic concentrations in igneous rocks are generally low. The concentration of arsenic in sedimentary rocks is typically in the range 5-10 mg/kg [55], which is slightly above the average terrestrial abundance of 1.5-3 mg/kg [2].

3.3. ARSENIC CHEMISTRY

Arsenic in aquatic system has an unusually complex and interesting chemistry with oxidation-reduction, ligand exchange, precipitation and adsorption reactions all taking place. Since it exhibits anionic behavior and forms anions in solution, arsenic does not form complexes with simple anions like Cl^- and SO_4^{2-} as do cationic metals. The complexation of arsenic by dissolved organic matter in natural environments prevents sorption and co-precipitation with solid-phase organics and inorganics, which results the mobility of arsenic in aquatic systems [56].

Arsenic is perhaps unique among the heavy metalloids and oxoanion-forming elements (e.g. As, Se, Sb, Mo etc.) in its sensitivity to mobilisation at the pH values typically found in groundwaters under both oxidizing and reducing conditions. The main arsenic species, as described earlier, present in natural waters are arsenate ions (oxidation state +V) and arsenite ions (oxidation state +III). However, As(V) ions are most prevalent in oxygen-rich waters and As(III) in anaerobic conditions like in well water. In many contaminated groundwaters As(III) and As(V) compounds coexist [7]. Both species have significant differences in the chemical behaviour. The dissociation reactions and the corresponding equilibrium constants of H_3AsO_4 and H_3AsO_3 are shown hereinafter in Table 3.1. [57]:

Table 3.1. Dissociation constants of arsenate and arsenite.

Speciation	Dissociation reactions	pK_a
As(V)	$H_3AsO_4 \leftrightarrow H^+ + H_2AsO_4^-$	2.24
	$H_2AsO_4^- \leftrightarrow H^+ + HAsO_4^{2-}$	6.69
	$HAsO_4^{2-} \leftrightarrow H^+ + AsO_4^{3-}$	11.5
As(III)	$H_3AsO_3 \leftrightarrow H^+ + H_2AsO_3^-$	9.2
	$H_2AsO_3^- \leftrightarrow H^+ + HAsO_3^{2-}$	12.1
	$HAsO_3^{2-} \leftrightarrow H^+ + AsO_3^{3-}$	13.4

However, the distribution of arsenic varies significantly depending on the pH and redox potential values. As(III) exists as non-dissociated at neutral and slightly acidic conditions and only at pH>8 considerable amount of anionic species are found. As(V), on the other hand, is almost completely dissociated and present in the form of monovalent, divalent and trivalent anions. Figs. 3.1 (a) and (b) show the speciation diagram of As(V) and As(III), respectively [58].

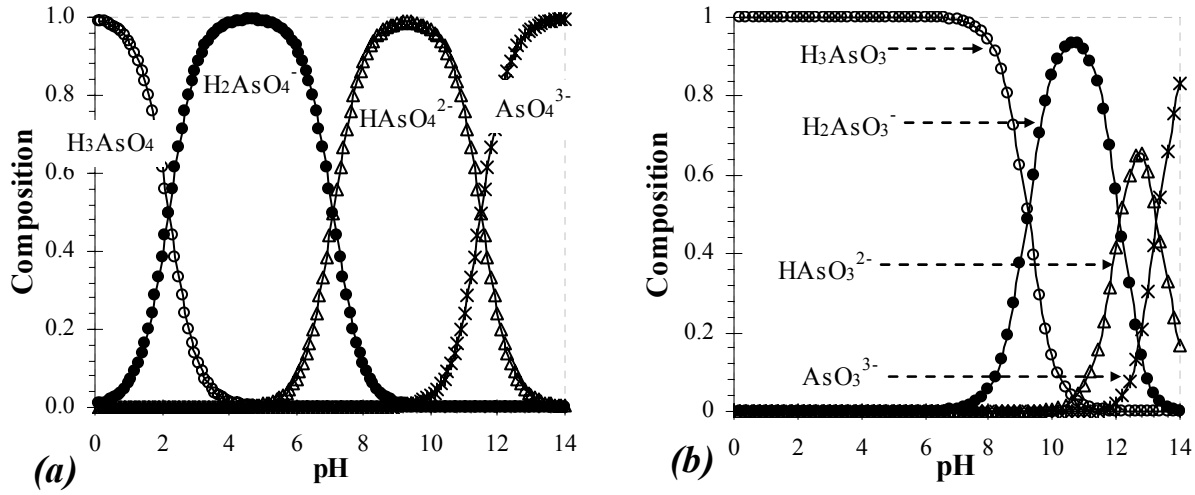


Fig. 3.1. Speciation diagram of (a) As(V) and (b) As (III).

3.4. ARSENIC IN WATER AND ITS HEALTH HAZARDOUS NATURE

Drinking water is generally obtained from numerous sources depending on local availability, which include surface water (rivers, lakes, ponds etc.), groundwater

(aquifers) and rain water. Incidents of arsenic contamination in water are quite common in the world [9,59]. It is generally recognized that the soluble inorganic arsenic are more toxic than its organic form and at the same time, the trivalent arsenic (arsenite) is more toxic than the pentavalent form (arsenate). Chronic exposure to arsenic concentration above 100 µg/l can cause vascular disorders, such as dermal pigments (Blackfoot dieses) and skin, liver and lung cancer, loss of apetite, nausea [10,11,59]. This differs from acute poisoning, which causes vomiting, abdominal pain and bloody "rice water" diarrhea [60,61].

To avoid hazards of arsenic, each country of the world defines the maximum amount of arsenic that it permits in drinking water. Since 1993 the World Health Organization (WHO) has recommended a maximum contaminant level for arsenic in drinking water of 10 µg/l yet the standard currently adhered to in Argentina, Bangladesh, China, India, Nepal and some other countries is 50 µg/l [9].

3.5. ARSENIC POISONING INCIDENTS ROUND THE WORLD

Incidents of arsenic poisoning have been reported from all over the world. Mandal and Suzuki [2] reviewed arsenic episodes round the world and its occurrence as well as toxicity. However, exposure of arsenic may come from natural sources, from industrial sources or from food and beverages. Following are some well-known cases of arsenic poisoning episodes:

3.5.1. Bangladesh

Arsenic episode in Bangladesh is well documented [62-64], which reports that about 25 million people of 2000 villages are in risk. Approximately 20.6% people of those areas are reported to be suffering from arsenicosis. The source of arsenic is oxidation of arsenic-rich pyrite or anoxic reduction of ferric iron hydroxides in the sediments to ferrous iron and thereby releasing the adsorbed arsenic to groundwater.

3.5.2. Japan

3.5.2.1. Fukuoka

Arsenic over permissible limit for drinking was detected in well waters on March 1994 in the southern region of Fukuoka Prefecture, Japan [65]. The highest

concentration was found to be 0.293 mg/l. The mechanisms of arsenic elution are thought to be involved with anion exchange with OH^- and reductive labialization of arsenic through conversion of arsenate to arsenite.

3.5.2.2. Nakajo

It is reported that in 1960 wastewater from a factory producing arsenic sulfide contaminated nearby well water in Nakajo, Nigata prefecture [66,67]. The concentration of arsenic in well water was 0.025-4.0 mg/l. Even though a small number of people drank the well water, various diseases related with arsenic ingestion such as hepatopathy, melanosis, hyperkeratosis was observed among the residents of that place.

3.5.2.3. Matsuo and Toroku

Matsuo and Toroku are two small mountain villages in the north of Miyazaki prefecture. Arsenious acid was produced in Toroku by roasting arsenopyrite ore [68]. On the other hand, white arsenic was produced in Matsuo by calcinating arsenopyrite at very primitive stone-made furnaces for nearly half a century since about 1920. In this system approximately 10% of As_2O_3 was lost as fumes through refining process. The arsenic-rich remains of calcinated ore were dumped into the river. Many mine workers and nearby residents died from acute and sub-acute arsenic poisoning. However, a 6-year follow-up study was carried out which revealed a high prevalence of malignant neoplasms in respiratory tract [69].

3.5.3. India

3.5.3.1. West Bengal

Around 1978 various aspects of arsenic ground water contamination and arsenicosis among people in some villages of West Bengal first came to the knowledge of Government of West Bengal. Various reports [70-72] reveal that about 6 million people of 2600 villages are affected by arsenic. They are found to suffer from arsenicosis, while the source of arsenic is oxidation of arsenic-rich pyrite or anoxic reduction of ferric iron and thereby releasing the adsorbed arsenic to groundwater.

3.5.3.2. Punjab and Hariyana

In several districts of Punjab and Hariyan, the arsenic concentration in water from wells and springs were reported to be higher (0.05-0.545 μg/l) than the accepted limit for drinking. The patients who consumed the water containing 0.545 ppm arsenic throughout the life were proved to suffer from non-cirrhotic portal fibrosis [73]. Since non-cirrhotic portal fibrosis and extra hepatic portal vein obstruction in adults are very common in India, it was testified that consumption of arsenic-contaminated water might have some role in the occurrence of such diseases [74]. The source of arsenic is, however, still unknown.

3.6. REMOVAL METHODS BY METAL-LOADED SORBENTS

Arsenic removal methods, in general, have been discussed earlier in section 2.2. In present section adsorptive removal techniques by using metal-loaded sorbents will be discussed since such sorbents are very prospective for arsenate and arsenite removal from water.

Metal-loaded sorbents were first described several decades ago to separate ligands of different coordination [75] but have been used recently for the treatment of water contaminated with toxic anions. One attractive feature of these sorbents is that most of the time, they overcome interferences with chloride and sulfate ions generally observed with strong anion exchange resins. Due to the strong interaction between the metal bound onto the polymer and arsenic, uptake capacities can also be increased. Strong cation exchange resins, porous polymers, chelating resins, or biopolymer gels have been used in the preparation of metal-loaded sorbents. Biopolymers like chitosan or alginate usually have a poor chemical and mechanical resistance. However, once metal ions are bound into the polymer matrix, they can act as a crosslinking agent and give the structure more strength [76]. The main advantages of chelating resins are that they are insoluble, nontoxic and chemically resistant as long as the chelating group bound to the polymer in not hydrolyzed in acidic or basic media. However, some metal-loaded sorbents, employed for arsenic removal, are discussed hereinafter.

Iron has been widely used for the preparation of metal-loaded sorbents. One of the first works reported by Yoshida et al. Ueno [77] investigated the removal of arsenic

ions on iron-loaded commercially available resin bearing hydroxybenzylnitilodiacetic groups. Matsunaga et al. [78] prepared a Fe(III)-loaded resin where iron was thought to be coordinated with one nitrogen and three oxygen of the chelating polymer. Since As(V) sorption decreased markedly at neutral pH, these resins were not so efficient as were in acidic media. However, for Fe(III)-loaded sorbents As(V) and As(III) were found to be adsorbed at acidic media and alkaline conditions, respectively.

Lanthanum-loaded resin has also been reported for effective adsorption of arsenic from water. Trung et al. [79] demonstrated that IDA resin loaded with La(III) could effectively preconcentrate very dilute solutions of As(V) and As(III). Wasay et al. [80] studied removal of hazardous anions from water using La(III)-impregnated alumima and found the selectivity order as such fluoride > phodphsate > arsenate > selenite. Like other metals, Y(III) [80] and Ce(III) [81] have been successfully loaded too to investigate the effect of arsenic removal.

Zirconium immobilization onto the sorbents has drawn much attention to the researchers. Zirconium oxide crystals were immobilized inside the pores of the polymer (polymethylmethacrylate beads) and positive results were obtained for arsenic removal [82].

So from such discussion it is summarized that a successful combination of metal ion and chelating polymer can be used for the effective removal of anions. Moreover, it is possible to attain the selectivity. The metal-loaded sorbents can also be used in a packed column.

Chapter 4

Experimental

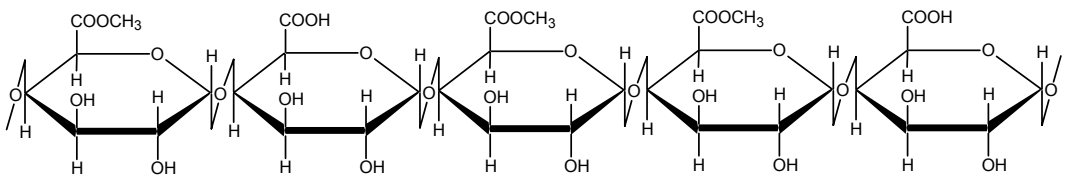
4.1. PREPARATION OF ARSENIC SOLUTION AND OTHER METAL SOLUTIONS

Arsenate and arsenite working solutions were prepared from sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) and arsenic trioxide (As_2O_3), respectively, by dissolving them in deionized water. Other aqueous metal solutions were prepared by dissolving corresponding analytical grade metal chlorides or nitrates in 0.1 M (M = mol/dm^3) hydrochloric acid. If required, 0.1 M *n*-2-hydroxyethylpiperazine-*n*-2-ethanesulphonic acid (HEPES), the buffering agent, was mixed at arbitrary volume ratio to adjust the pH of the solution.

4.2. PREPARATION OF THE GEL

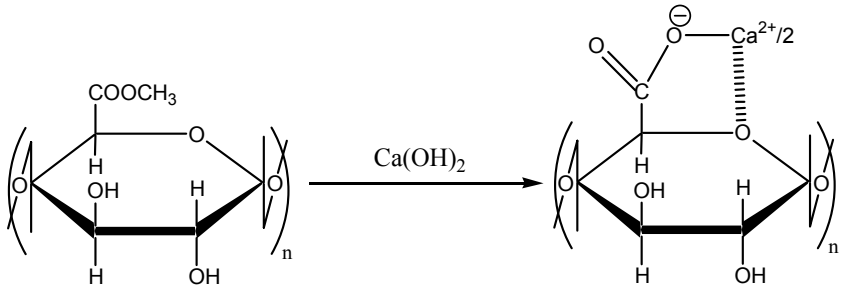
4.2.1. Preparation of saponified orange waste (SOW) gel

Crude orange waste, donated by JA Saga Beverage Ltd., Japan, was stored in a refrigerator at about -20°C. Orange waste consists of pectin, cellulose, hemicellulose, limonene and many other low molecular weight compounds [83]. Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plants tissues. It is the methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 galacturonic acid. The degree of esterification affects the gelling properties of pectin. The structure of pectin (Scheme 4.1) has three methyl ester forms (-$COOCH_3$) for every two carboxyl groups (-COOH); hence it has 60% degree of esterification.



Scheme 4.1. Chemical structure of pectin.

However, methyl ester groups, present in pectin, were saponified with calcium hydroxide under highly alkaline conditions to convert them into carboxyl groups according to the reaction as follows (Scheme 4.2):



Scheme 4.2. Saponification of methylated ester part of pectin.

About 100 g of orange waste was taken along with 8 g of $Ca(OH)_2$ and crushed into small particles by using a HITACHI VA-10 juice mixer for about 15 minutes at room temperature. Calcium hydroxide facilitates not only the saponification process but also bleaching out of chlorophyll pigments and other low molecular weight compounds that may hinder the adsorption process.

The crushed orange waste suspension was transferred to a beaker, a substantial amount of deionized water added and the mixture stirred for 24 h at about 200 rpm in order to further facilitate the saponification. The initial pH of this suspension was maintained at around 12.5 by adding sodium hydroxide solution. After stirring, the suspension was repeatedly washed with deionized water until neutral pH by means of decantation and finally filtered to obtain a wet gel, which was dried in a convection oven for about 48 h at 70ºC. The dried gel was further ground into smaller particles. The gel prepared by this method is identified as SOW gel hereafter, which stands for saponified orange waste. The specific surface area of this gel was measured as 7.25 m^2/g by using Belsorp 18PLUS-SP (BEL JAPAN INC.) according to the BET method while leading pore size was found to be mesoporous with an average pore diameter of 14.3 nm.

However, since the measured amount of exchangeable hydrogen ion in the gel was much higher than the amount of the pectic acid content in the orange waste as reported in the literature [83], it is considered that some of cellulose and hemicellulose was partially oxidized to pectic acid analogues by means of alkaline wet oxidation [84].

4.2.2. Preparation of H^+-form SOW gel and determination of the exchangeable cation

The saponified orange waste was washed with 0.1 M hydrochloric acid solution for 2 h. The suspension was then washed by deionized water till neutrality. The H^+-form gel thus obtained was dried and used to evaluate the maximum exchangeable cations. About 50 mg of dried H^+-form gel and 30 ml of 0.01 M of sodium hydroxide solutions were put into 50 ml conical flasks. Thus five samples were prepared and equilibrated for 24 h at 30ºC. The decrease in hydrogen ion concentration in each conical flask was evaluated by titrating the filtrate with 0.01 M hydrochloric acid solution using phenolphthalein as an indicator.

4.2.3. Preparation of metal-loaded SOW gel

The SOW gel does not adsorb anions because it is a cation exchanger, which adsorbs a range of cations. This property has allowed SOW to make an adsorption gel after loading metal ions. Consequently, the SOW gel was loaded with various metal ions such as, La(III), Ce(III) and Zr(IV) for the subsequent adsorption tests for arsenic. To prepare the La(III)- and Ce(III)-loaded SOW gel, 5 g of dry SOW was first equilibrated with 500 ml of 0.01 M metal solution for 24 h at pH 5. The suspension was then washed and filtered with deionized water until neutral pH and finally dried at 70ºC. Thus La(III)- and Ce(III)-loaded SOW gels were prepared. On the other hand to prepare the Zr(IV)-loaded SOW gel, 3 g of SOW gel was equilibrated with 500 ml of a 0.1 M zirconium solution at pH 2.11 for 24 h. The gel was then filtered and washed as usual with deionized water until neutral pH, followed by drying in vacuum until constant weight. The amount of metal ions loaded on the SOW gel was calculated from the difference in the concentration of the solution before and after loading. For all cases the adsorption gels were finally sieved to produce a particle size fraction of between 75 and 150 μm for the adsorption tests.

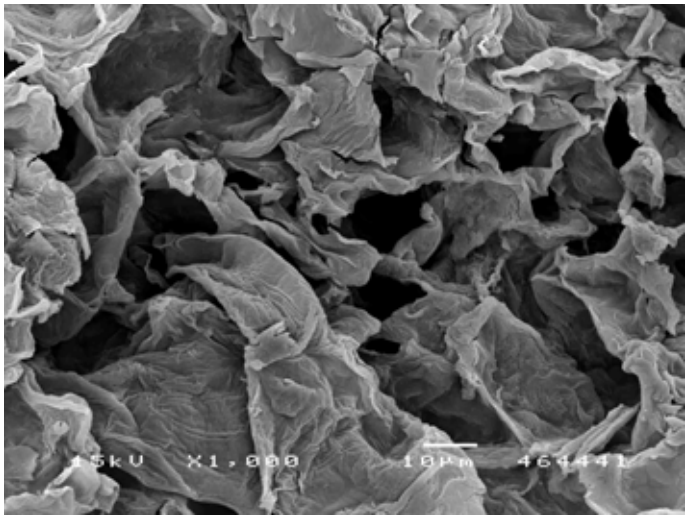
4.3. EFFECT OF SOLID/LIQUID RATIO

Effects of solid/liquid ratio tests were carried out by varying the amount of adsorption gels and keeping the concentration as well as amount of solution constant.

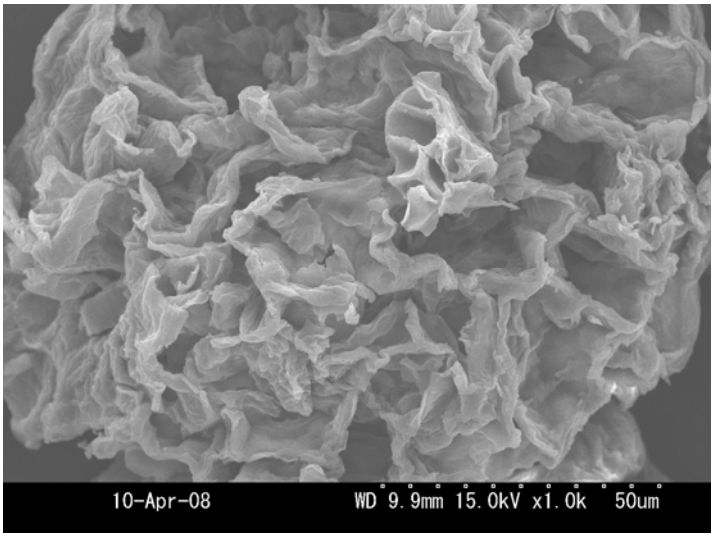
Approximately 10, 15, 25, 30, 50 and 80 mg of metal-loaded gel was taken into six 50 ml stoppered conical flasks. In each of these flasks 15 ml of 10 mg/l arsenic solution were poured. The initial pH of the arsenic solution was kept constant at 6.5. The flasks were then shaken in a thermostated shaker (THOMAS thermostatic shaking incubator AT24R) maintained at 30ºC and 138 rpm for about 24 h to attain equilibrium. The suspensions were filtered and the % adsorption was measured from the decrease in the arsenic concentration.

4.4. SURFACE ANALYSIS OF GELS

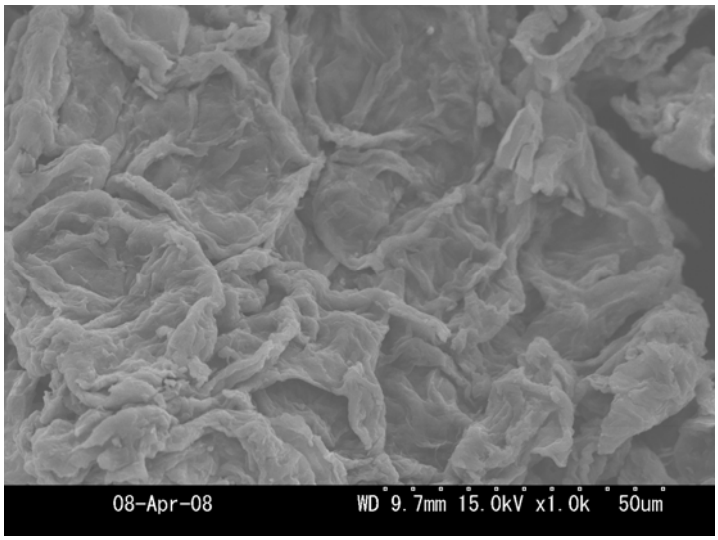
The surface morphology was observed by a scanning electron microscope (HITACHI S-3000N). However, to understand and analyze the surface morphology of the gel, SEM images of La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels has been taken at 1000X magnification as shown in Figs. 4.1 (a)-(c). The gel is found to be porous in structure. Since micro and meso pores are observed on the surface of the gel, significant adsorption is likely to occur. However, the adsorption of arsenic is predicted to occur with the ligand exchange between hydroxyl ions or water molecules and arsenic anions.



(a) 1000X magnification, scale = 10 μm, acceleration voltage = 15 kV.



(b) 1000X magnification, scale = 50 μm, acceleration voltage = 15 kV.



(c) 1000X magnification, scale = 50 μm, acceleration voltage = 15 kV.

Fig. 4.1. Scanning Electron Microscope (SEM) images of (a) La(III)-loaded, (b) Ce(III)-loaded and (c) Zr(IV)-loaded SOW gels.

4.5. EFFECT OF pH ON ARSENIC REMOVAL

Batch-wise adsorption tests for arsenic removal were carried out to examine the adsorption behavior of arsenic onto different metal-loaded SOW gels. Adsorption of arsenic as a function of pH was examined in a series of experiments where the initial arsenic concentration was maintained constant at varying pH. The percentage adsorption (*R*%) was calculated according to the following equation (Eq.1):

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where, C_i and C_e are initial and equilibrium concentrations (mg/l), respectively. However, pH of the solution was adjusted by adding small amounts of NaOH or HCl. From such experiments the pH at which the maximum arsenic adsorption occurs, can be found. All batch adsorption experiments were carried out in 50 ml stoppered conical flasks by taking 25 mg (dry weight) of the gel together with 15 ml of arsenic solution. The flasks were then shaken in a thermostated shaker maintained at 30ºC and 138 rpm for about 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1-µm filter paper and their equilibrium concentrations were measured.

4.6. ADSORPTION ISOTHERMS OF ARSENIC

To evaluate the adsorption isotherms, the adsorption tests were carried out individually for arsenate and arsenite in the concentration range of 5-800 mg/l for various metal-loaded SOW gels at their optimum pH values. The adsorption isotherms for As(V) and As(III) were measured at pH values 6.5 and 10, respectively, for both La(III)- and Ce(III)-loaded gels. On the other hand, for Zr(IV)-loaded SOW gel system, pH 3 and 10 was selected for adsorption of As(V) and As(III), respectively. However, the amount of adsorption (q) was calculated according to the following equation (Eq. 2):

$$q = \frac{C_i - C_e}{W} \times V \quad (2)$$

where, q is the amount adsorbed (mg/g), W and V are weight of adsorption gel (mg) and volume of aqueous solution (ml), respectively. However, reproducibility of all these batch adsorption experiments as well as column-mode experiments, which will be described later (section 4.8), was confirmed by carrying out the same adsorption tests in triplicate and the mean value was taken.

4.7. KINETIC STUDIES

Experiments with La(III)-loaded SOW gel for the adsorption of As(V) and As(III) were performed to determine the adsorption equilibrium time and adsorption kinetics.

The amount of 317 mg La(III)-loaded SOW gel was placed in a 200 ml Erlenmeyer flask and arsenic solution (190 ml) was poured into the flask. This will provide a solid/liquid ratio of 1.67 mg/ml. The Erlenmeyer flask was placed in a water bath and a constant temperature (30°C) was maintained throughout the experiment. The suspension was stirred with a magnetic stirrer at approximately 140 rpm. The Erlenmeyer flask is properly sealed with parafilm (American National Can Company, USA) to avoid loss due to evaporation. However, three different sets with arsenic concentration of 15, 45 and 90 mg/l were examined. The experiments were carried out at optimum pH values to obtain the best adsorption e.g. 6.5 for As(V) and 10 for As(III). While stirring, the sample (3~5 ml) was taken from the suspension successively at 0, 10, 20, 30, 60, 90, 120, 240, 480, 900, 1200 and 1440 min of contact time between the gel and the arsenic containing solution. At the end of each contact time, the suspension was immediately filtered through a 1 μm filter paper and the filtrate analyzed. The amount of arsenic adsorbed at time t, q_t (mg/g of dry gel), was calculated from the mass balance between initial concentration and concentration at time t. The data were used to analyze the adsorption rates of arsenic onto the La(III)-loaded SOW gel.

At the same way, kinetic studies of As(V) adsorption using Zr(IV)-loaded SOW gel was also performed at pH 3 with initial concentrations of 25, 50, 75 and 100 mg/l.

4.8. DYNAMIC STUDIES: ADSORPTION FOLLOWED BY ELUTION

Dynamic tests for the adsorption of target hazardous anions (arsenate and arsenite) were individually carried out by using the La(III)- and Zr(IV)-loaded SOW gels at 30°C in a transparent glass column of 0.8 cm inner diameter and 20 cm high fitted with a glass filter at the bottom as shown in Fig. 4.2. The entire column was equipped with a jacket surrounding the column to keep the temperature constant at 30°C. Approximately 150 mg of the gel was first adequately soaked in deionized water to facilitate swelling and then packed into the column. The test solution, containing arsenic was percolated through the column using an EYELA model MP-3N micro tube pump. The pH of the feed solution was maintained as the optimum pH to obtain best adsorption. Prior to the start of the dynamic studies, the column was conditioned by passing water at the same pH for 24 h. A fraction collector (BIORAD Model 2110)

was used to collect the fractions of effluent at definite intervals of time in 8 ml plastic tubes for the measurement of the arsenic concentration. After the complete breakthrough, elution tests for As(V) and As(III) were carried out using 1 M HCl and 1 M NaOH, respectively. Here, the column was washed with de-ionized water to expel any unbound arsenic. At the same time, it facilitates the regeneration of the packed material.

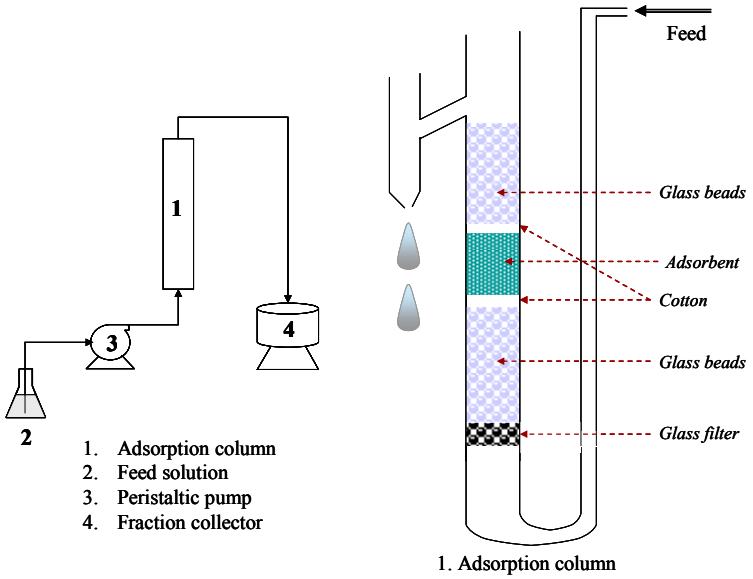


Fig. 4.2. Schematic diagram for the column experiments.

4.9. ANALYSES

The pH of the solutions was measured using either a DKK-TOA model HM-25G pH meter or an ORION model 720 pH meter, which were calibrated on a daily basis. The concentrations of all metal ions as well as arsenic were measured by using a Shimadzu model ICPS-8100 inductively coupled plasma-atomic emission spectrometer (ICP/AES). The linearity of calibration ranges from 2 µg/l up to 1000 µg/l with a detection limit of about 1 µg/l for each species measured. Standard solutions of arsenic and other metal ions (Wako Pure Chemical Industries, Ltd., Japan) of 1000 mg/l were diluted to the desired concentration and used for ICP/AES calibration. HITACHI S-3000N Scanning Electron Microscope was used to analyze surface of the gels.

Chapter 5

Results and Discussion

5.1. EXCHANGEABLE CAPACITY OF SOW GEL

The amount of total exchangeable cation was evaluated to be 2.69 mol H^+/kg for SOW gel [85]. Dhakal et al. carried out a similar analysis for pure pectic acid gel and found the amount of exchangeable cations to be 5.65 mol/kg [53]. These results suggest that a comparatively much cheaper adsorbent having the same functional group (-COOH) can be used for adsorption purposes instead of using pure pectic acid.

5.2. LOADING OF METAL IONS ONTO SOW GEL

The effect of the equilibrium pH on the adsorption of La(III), Ce(III) and Zr(IV) onto the SOW gel is illustrated in Fig. 5.1, which demonstrated that maximum adsorption of La(III) and Ce(III) occurred between pH 5.5 and 6.5 while that of Zr(IV) took place from pH 1.5 to 6.5. Above pH 6.5, metals were hydrolyzed to form their hydroxides, especially at concentrations greater than 1 mM. Consequently, pH 5.5 was selected for loading of La(III) and Ce(III) onto the gel whereas for Zr(IV) the selected pH was 2.11.

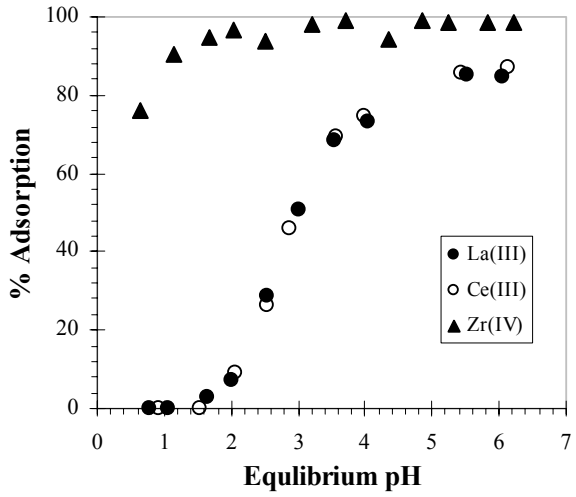


Fig. 5.1. Effect of pH on different metal adsorption onto SOW gel. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 1 mM, t = 24 h, T = 30ºC.

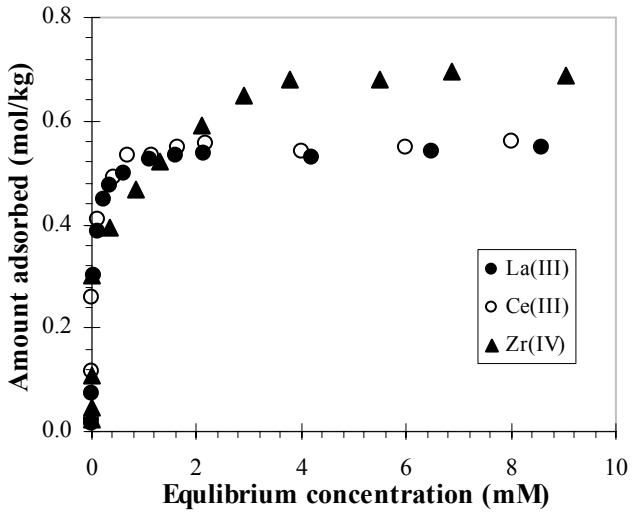


Fig. 5.2. Adsorption isotherms of different metals.

Figure 5.2 illustrates the adsorption isotherms for La(III), Ce(III) and Zr(IV) metals, which shows that the adsorption increases with increasing metal concentration and tends to approach a constant value. The adsorption isotherms for all metals were found to be in accordance with the Langmuir isotherm, from which the loading capacities of the gel were evaluated as 0.55 mol-La(III)/kg, 0.55 mol-Ce(III)/kg and 0.70 mol-Zr(IV)/kg. The higher loading capacity in case of Zr(IV) is due to its smaller ionic radius.

5.3. EFFECT OF ADSORBENT DOSE ON ARSENIC ADSORPTION

In order to obtain the optimum solid/liquid ratio the amount of adsorption gel was varied keeping the concentration and amount of solution constant. Fig. 5.3 shows the variation of arsenic adsorption onto La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels as a function of adsorbent dose (0.6~6 mg/ml). It can be observed that the % adsorption of As(V) increases with the increase in adsorbent dose. This may happen due to the increased number of active sites with an increase in amount of adsorbents. After a certain adsorbent dose, the adsorption does not increase significantly with further increase in solid/liquid ratio because the sites available for adsorbing given amount of As(V) are in excess. Since, the increase in % adsorption is very insignificant at high adsorbent dose, 1.67 was taken as an optimum solid/liquid ratio for all gels.

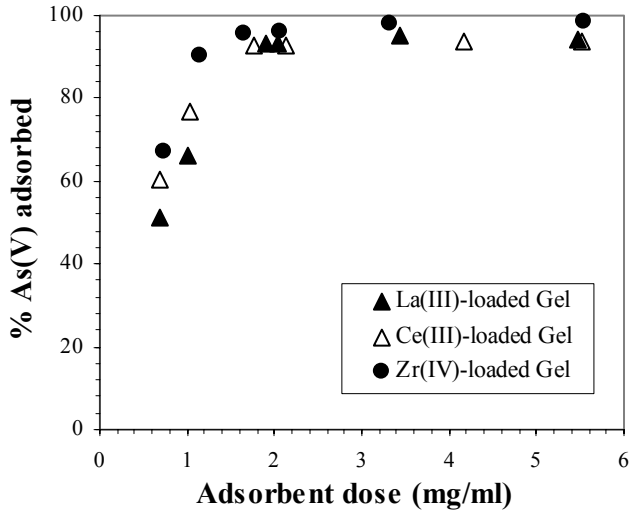
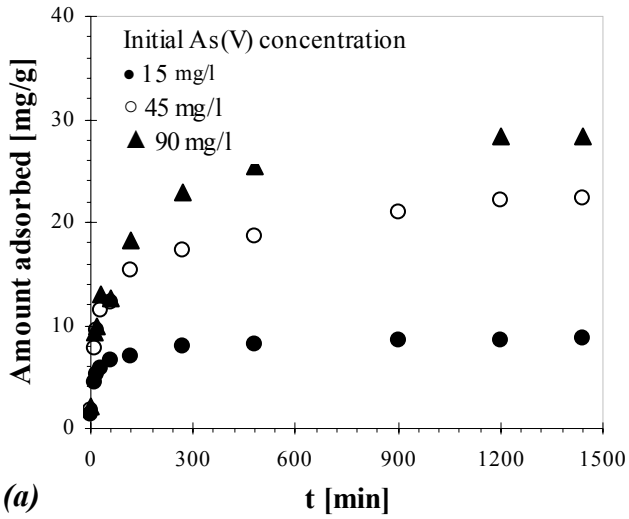
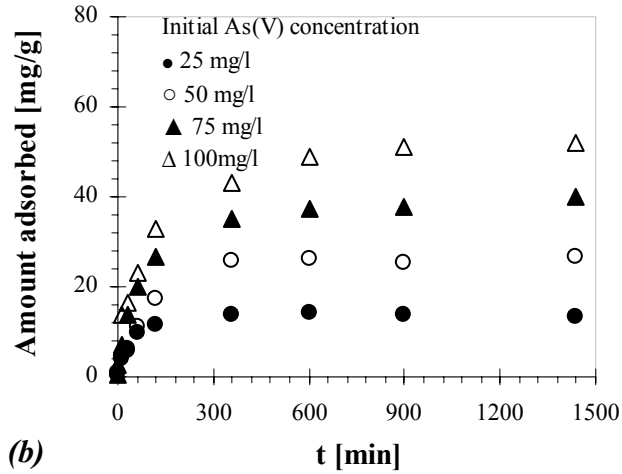


Fig. 5.3. Effect of adsorbent dose on arsenic adsorption. Conditions: C_{in} = 10 mg-As(V)/l, solution = 15 ml, t = 24 h, T = 30°C.

5.4. KINETIC STUDIES

In order to obtain kinetic data for As(V) and As(III) adsorption onto the metal-loaded gels, the variation of the arsenic concentration with time was measured. The rate of As(V) uptake by the La(III)- and Zr(IV)-loaded gels has been depicted in Figs. 5.4 (a) and (b), respectively, while Fig. 5.4 (c) shows the rate of As(III) adsorption onto the La(III)-loaded SOW gel. These figures show that the amount of arsenic adsorption increases rapidly with increasing shaking time and it tends to approach a constant value after a certain shaking time depending on the initial arsenic concentration. It also shows that adsorption is rapid during the initial adsorption stages and then approaches equilibrium regardless of the initial arsenic concentration. However, 24 h was found to be enough for obtaining equilibrium. Consequently 24 h was determined as optimum shaking time for the subsequent adsorption tests. A similar observation was reported by Singh et al. [86] for As(V) adsorption on hematite and feldspar. However, the initial rapid step may be attributed to diffusion controlled sorption onto the gel [87]. All curves shown in Figs. 5.4 (a), (b) and (c) are single, smooth and continuous leading to saturation, suggesting a monolayer coverage of the surface of the gel [88,89].





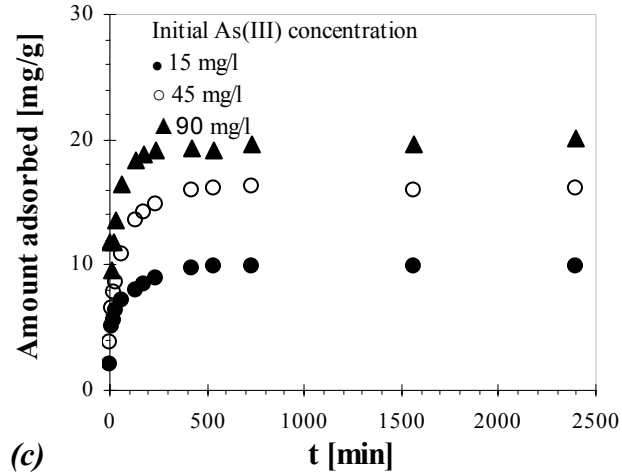


Fig. 5.4. Effect of shaking time and initial arsenic concentration. Conditions: S/L ratio = 1.67 mg/ml, T = 30°C.

Lalvani et al. [90] proposed an empirical rate expression described by Eq. 3 for the adsorption kinetics of hexavalent chromium on a carbon adsorbent.

$$R = k_t t^m \tag{3}$$

where R and t denote the % removal of solute from the aqueous solution and contact time, respectively, and k_t and m are constants. Figure 5.5 shows the plot of $log_e R$ against $log_e t$ for the data shown in Fig. 5.4(a) according to Eq. 3. As expected, fairly linear plots are obtained for all three different initial arsenate concentrations. The numerical values of m are calculated to be 0.32, 0.30 and 0.29 for initial concentrations of 15, 45 and 90 mg-As(V)/l, respectively. According to Lalvani et al. [90], the reaction order (n) is expressed as follows (Eq. 4):

$$n = m^{-1} - 1 \tag{4}$$

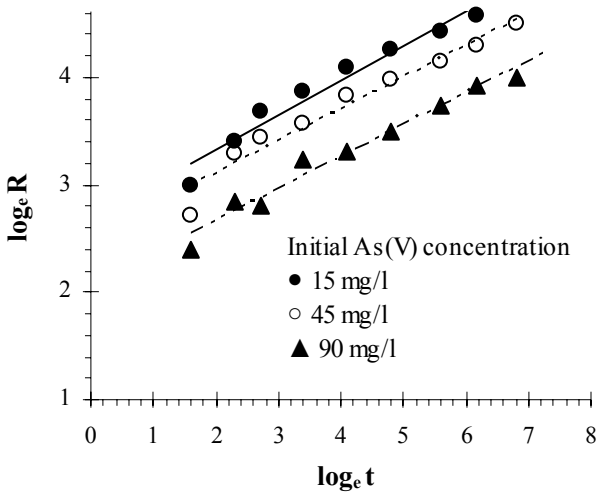


Fig. 5.5. Logarithmic plot of As(V) removal efficiency versus time. Conditions: S/L ratio = 1.67 mg/ml, T = 30°C, pH = 6.5.

From Eq. 4, the reaction order was evaluated to be 2.08, 2.33 and 2.35 for 15, 45 and 90 mg/l initial As(V) concentrations, respectively. Therefore, it may be assumed that the kinetics of arsenate adsorption can be represented by a second order rate equation. Consequently, in the present work, the adsorption rate has been analyzed based on the pseudo-second-order rate equation proposed by Ho and McKay [91], expressed as follows.

$$dq_t/dt = k(q_e - q_t)^2 \tag{5}$$

where k is the rate constant [g/(mg·min)], and q_t and q_e denote the amount of arsenic adsorbed (mg/g) at any time t and at equilibrium, respectively. Integration of Eq. 5 within the initial and boundary conditions gives the relationship between q_t and t described by Eq. 6.

$$t/q_t = t/q_e + 1/kq_e^2 \quad (6)$$

It is to be noted that k and q_e are evaluated from the intercept and slope for the linear relationship between t/q_t and t (from Eq. 6). However, these kinetic parameters have also been evaluated from nonlinear regression by using XLSTAT, a statistical analysis package, developed by Kovach Computing Services [92]. The kinetic parameters thus evaluated and the correlation coefficients calculated at different concentrations are listed in Table 5.1. The values of kinetic parameters obtained from nonlinear regression resemble to that of linear regression. Since the adsorption rate process follows a pseudo-second-order model, it can be surmised that a chemisorption process may have taken place for arsenic sorption onto the gel [91,93]. It is noteworthy to mention here that, an attempt was taken to fit the kinetic data using first order kinetic model, but it did not match well.

Table 5.1. Kinetic parameters for the adsorption of arsenic by the La(III)- and Zr(IV)-loaded SOW gels.

Species	*Gel*	C_{in} *(mg/l)*	$q_{e,exp.}$ *(mg/g)*	*Pseudo-2nd-order*			*Non-linear regression*	
				k [g/(mg·min)]	R^2	$q_{e,cal}$ *(mg/g)*	$q_{e,cal}$ *(mg/g)*	R^2
As(V)	La(III)-loaded SOW gel	15	8.5	6.19×10^{-3}	0.99	8.8	8.41	0.963
		45	22.1	1.07×10^{-3}	0.99	22.5	21.07	0.958
		90	28.4	7.54×10^{-4}	0.99	29.2	28.13	0.974
As(V)	Zr(IV)-loaded SOW gel	25	13.8	4.36×10^{-3}	0.99	13.9	14.64	0.985
		50	26.5	5.63×10^{-4}	0.99	27.8	29.43	0.986
		75	38.5	4.53×10^{-4}	0.99	40.9	41.25	0.999
		100	51.5	3.10×10^{-4}	0.99	52.9	53.96	0.992
As(III)	La(III)-loaded SOW gel	15	7.8	5.44×10^{-3}	0.99	8.0	7.64	0.957
		45	15.9	3.42×10^{-3}	0.99	16.3	16.29	0.961
		90	19.6	3.3×10^{-3}	0.99	20.1	19.77	0.985

5.5. IR SPECTRUM STUDIES OF Zr(IV)-LOADED SOW GEL BEFORE AND AFTER As(V) ADSORPTION

IR analysis permits spectrophotometric observation of the adsorbent surface in the range of 400~4000 cm^{-1} and serves as a direct means for the identification of functional groups on the surface. An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface groups that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has taken place [94]. However, FT-IR spectra of the Zr(IV)-loaded SOW gel, before and after As(V) adsorption, were taken (Fig. 5.6) in order to understand the structural change as well as the involvement of main functional groups in arsenic adsorption. Since the structure of the gel is complex, a complete diagnosis of the spectra seems to be difficult to elucidate. An attempt, however, has been made to explain the structural changes during the adsorption of arsenic.

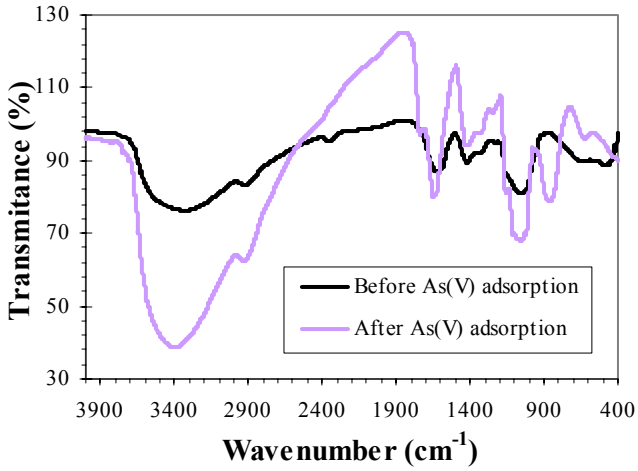


Fig. 5.6. FT-IR spectra of Zr(IV)-loaded gel taken before and after As(V) adsorption.

Both spectra show the O-H stretching region at around 3400 cm^{-1}. However, a new band at 883 cm^{-1}, which corresponds to As-O stretching vibration, confirms arsenic adsorption onto the metal-loaded SOW gel. A similar phenomenon has been reported for arsenic adsorption using activated carbon [95]. Carboxyl group is supposed to be a characteristic group of pectic acid, which is the key compound found in orange waste for making adsorption gel. The asymmetrical C=O stretching band for carboxylic group at 1617 cm^{-1} observed for Zr(IV)-loaded SOW gel has shifted to 1651 cm^{-1} after arsenic adsorption with a different magnitude. These band changes indicate the

involvement of carboxyl group in arsenic adsorption, probably through chelation/complexation [96].

5.6. EFFECT OF pH ON THE ADSORPTION OF As (V and III)

The solution pH is an important parameter for adsorption of arsenic as well as water treatment process because it affects the speciation of the solute in water. In this work, a wide range of pH (1~13) has been studied to know the effect of pH on arsenic removal from aqueous solutions.

The effect of equilibrium pH on arsenic removal by using the La(III)-, Ce(III)- and Zr(IV)-loaded gels has been depicted in Figure 5.7, which shows that As(V) is effectively adsorbed by using the La(III)- and Ce(III)-loaded SOW gels over a pH range from 6 to 9.5. However, pH 6.5 was selected for further batch adsorption tests for aforementioned two gels. According to Wasay et al., La(III) and Y(III) impregnated alumina can effectively remove As(V) in the optimum pH range of 6 to 8 [80], compared with which the adsorption onto the La(III)- or Ce(III)-loaded SOW gel has a wider optimum pH range for As(V) removal, which should be of great advantage for practical operation. The Zr(IV)-loaded SOW gel, on the other hand, has shown maximum adsorption in weakly acidic conditions as well as near neutral region i.e. at pH 2 to 6; even though more than 80% adsorption is still observed up to pH 9.5. In this case pH 3 was selected for carrying out further adsorption tests.

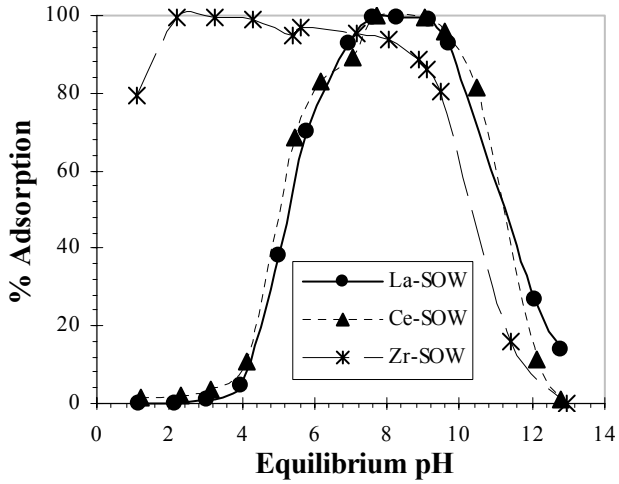


Fig. 5.7. Effect of pH on the adsorption of As(V) onto La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 4 mg/l (for La(III)- and Ce(III)-loaded gel), 20 mg/l (for Zr(IV)-loaded gel), t = 24 h, T = 30°C.

Arsenic(V) can exist in different ionic species depending on solution pH [58]. The dominant species in the above mentioned pH range are $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions which can be adsorbed on the gel by substituting hydroxyl ions from the coordination sphere of the loaded lanthanides or zirconium. Since the lanthanide and zirconium ions tend to be extensively polymerized and hydrolyzed even at very low concentration and they convert into $[Ln(H_2O)_n]^{3+}$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and/or $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species [97]; a lot of hydroxyl ions are therefore available for ligand exchange with arsenic anions.

In contrast to the removal of As(V), adsorption of As(III) was the most favorable at pH 9~11 for both the La(III)- and Ce(III)-loaded SOW gels and pH 9~10 for Zr(IV)-loaded-SOW gel as shown in Fig 5.8. Hence, pH 10 was selected for further adsorption tests of As(III) from water using all kinds of gels. In solution, up to pH 8, arsenite exists principally as undissociated H_3AsO_3 [58], which accounts for the lack of adsorption. The predominant monoanionic ($H_2AsO_3^-$) and neutral (H_3AsO_3) species are thus considered to be responsible for the adsorption of As(III) by substitution of the hydroxyl ions and/or water molecules in the above mentioned pH range.

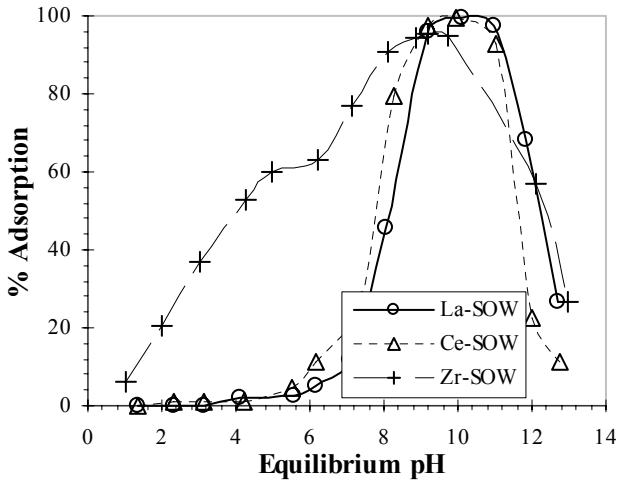
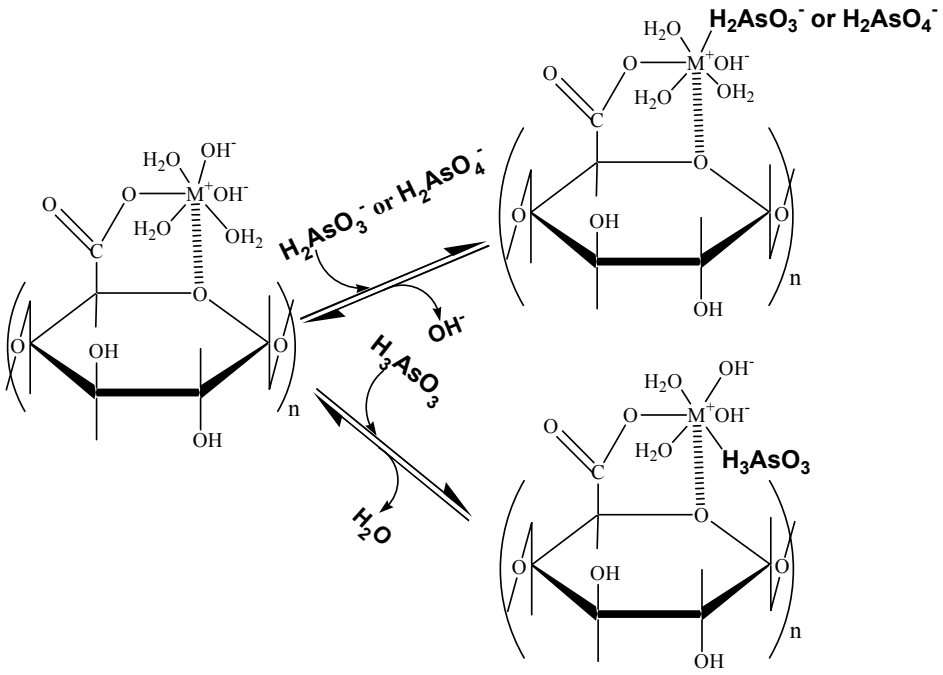


Fig. 5.8. Effect of pH on the adsorption of As(III) onto La(III)-, Ce(III)- and Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 4 mg/l (for La(III)- and Ce(III)-loaded SOW gel), 20 mg/l (for Zr(IV)-loaded SOW gel), t = 24 h, T = 30°C.

Arsenate and arsenite are inferred to be adsorbed onto the gel according to the ligand exchange reaction as shown in Scheme 5.1. Ligands involved in such exchange

processes may be hydroxyl ions or neutral water molecules existing in the metal coordination spheres. These mechanisms have been further supported by the fact that the pH of the solution had been increased or almost no change had taken place after arsenic adsorption in the present experiments. Similar mechanisms have been reported for the adsorption of As(V) on aluminum-loaded Shirasu-zeolite [44], As(V) as well as As(III) on Fe(III)-loaded crosslinked seaweed gel [98] and fluoride on various La(III)-loaded adsorbents [99]. Figures 5.7 and 5.8 also show that % removal of arsenic decreases with a further increase in pH. The decrease in arsenic adsorption can be attributed to the competition between hydroxyl ions, predominant at higher pH, and arsenic species for the adsorption sites.



Scheme 5.1. Inferred mechanism of ligand exchange for arsenic adsorption onto the metal-loaded SOW gels.

Different sorption behavior is observed for the Zr(IV)-loaded SOW gel compared to the La(III)- and Ce(III)-loaded SOW gels, which may be attributed to the loaded metal ions and their physicochemical properties. The extremely low value of the solubility product of $Zr(OH)_4$ compared to those of $La(OH)_3$ and $Ce(OH)_3$ may have an effect on the adsorption of arsenic. Since lanthanides have coordination numbers of 6, 8, 9 [100] or even more, e.g. 10 or 11, which allow to take various geometries while zirconium has a coordination number of 4, 6, 8 [97], the differences in the

coordination spheres may also be responsible for the different adsorption behavior between the Zr(IV)-loaded and lanthanides(III)-loaded SOW gel systems.

5.7. EFFECT OF OTHER COMPETING ANIONS ON THE ADSORPTION OF ARSENATE

Several anions may exist in the water which can compete with the arsenic for the available adsorption sites of the gel. The major co-existing anions e.g. chloride, carbonate, sulfate and phosphate have been tested to determine their effect on arsenic adsorption in this study. To assess the effect of foreign anions on arsenic removal by the Zr(IV)-loaded SOW gel, batch adsorption tests were carried out by equimolar (≈ 0.27 mM) addition of other anions such as chloride, sulfate and carbonate. Figure 5.9 shows the effect of other anions on the adsorption of As(V), which suggests that such anions hardly interfere with As(V) adsorption. Similar results were also found for As(III) adsorption as well.

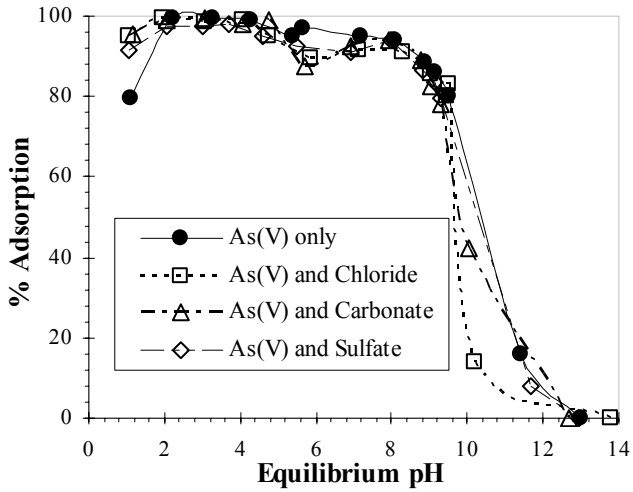


Fig. 5.9. Effect of other anions on As(V) removal on Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, C_{in} of each anion = 0.27 mM, t = 24 h, T = 30ºC.

Phosphate, on the other hand, has exhibited a strong effect on adsorption of arsenate. The La(III)- and Zr(IV)-loaded SOW gels were tested to find the effect of presence of phosphate on arsenate adsorption. The adsorption capacity decreases with the increase in phosphate concentration for both gels. In case of La(III)-loaded SOW gel, shown in Fig. 5.10 (a), 51, 75 and 80% decreases in adsorbed amount of arsenate

occurred with the presence of 0.7, 1.1 and 2.3 mM of phosphate. A similar behavior has also been observed with the Zr(IV)-loaded SOW gel as shown in Fig. 5.10 (b).

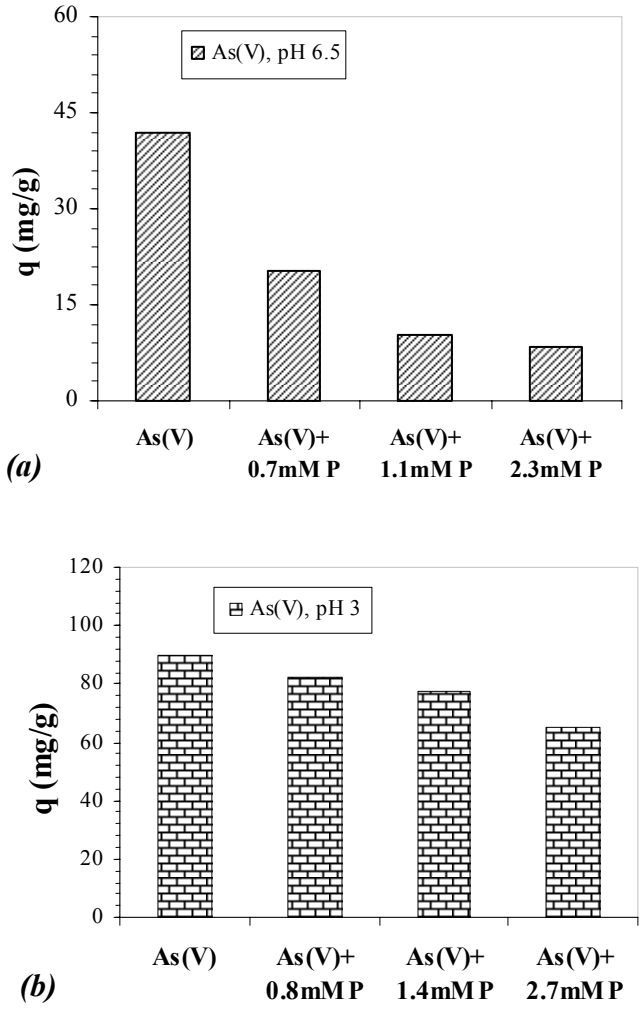
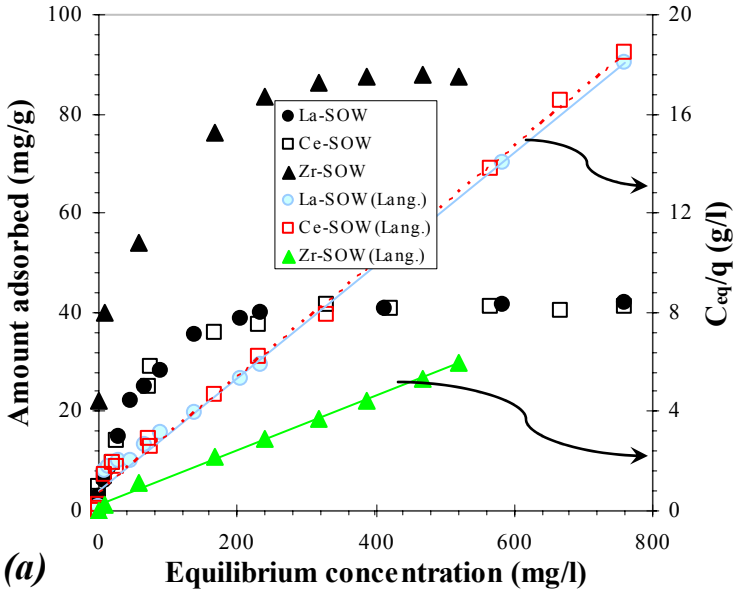


Fig. 5.10. Effect of phosphate on As(V) removal on (a) La(III)-loaded SOW gel and (b) Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

Phosphate is found to be a strong interfering ion possibly due to its higher affinity to the gel compared to arsenate ion and the decrease in arsenic adsorption is attributed to the competition between phosphate and arsenate anions. Phosphate is likely to be adsorbed onto the gel through the formation of surface complexes with the surface hydroxyl group [101]. Suzuki et al. [82] reported an analogous behavior while removing arsenic using Amberlite XAD-7, a polymer resin.

5.8. ADSORPTION ISOTHERMS

In order to determine the adsorption capacity for arsenic on the metal-loaded gels, and to diagnose the nature of this adsorption, the equilibrium adsorption isotherm is of fundamental importance. The equilibrium adsorption capacities of the gels were measured at varying concentrations of arsenic. Figures 5.11 (a) and (b) show the adsorption isotherms of As(V) and As(III), respectively, under the conditions given in the figure legends. At low arsenic concentration the adsorption of both As(III) and As(V) increases with increasing equilibrium concentration, which is followed by a plateau, indicating that the adsorption of both arsenic species onto the gel has taken place according to the Langmuir adsorption isotherm. From the values of the plateaus, the maximum adsorption capacities for As(V) adsorption were determined to be 43, 43 and 88 mg/g for the La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels, respectively, while the corresponding As(III) adsorption capacities were 42, 42 and 130 mg/g. Although it is difficult to compare the gels tested in this study directly with other adsorbents because of different experimental conditions applied, still it is found that the adsorption capacities for arsenic adsorption on the prepared gels are reasonably higher than that of other adsorbents (Table 5.2), which justifies the chemical modification of orange waste. From the view point of high arsenic adsorption capacity, the metal-loaded gel; Zr(IV)-loaded SOW gel in particular, is expected to be employed commercially for the removal and recovery of arsenic from aqueous solution contaminated with arsenic.



(a)

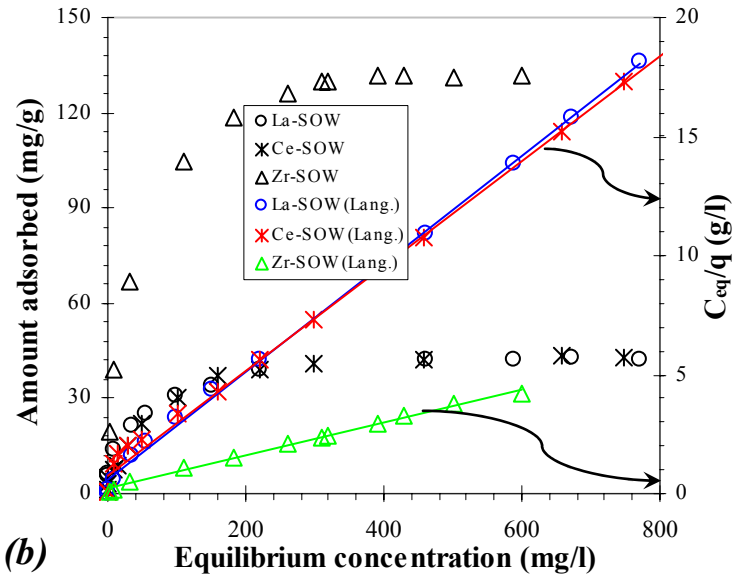


Fig. 5.11. Adsorption isotherms for (a) As(V) and (b) As(III) on different metal-loaded gels. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

The linear plots according to the Langmuir equation in Fig. 5.11 nicely fit with the experimental data with an excellent correlation coefficients (>0.99), which signify the homogeneous distribution of active sites on the gel surface [102]. Non-linear regression analysis using XLSTAT, a statistical package, has also been performed to obtain the model parameters. It was found that the values obtained from such nonlinear regression were nearly the same as that obtained from linearization method. In these adsorption tests, leakage of metal ions from the gel was very insignificant under the mentioned experimental conditions.

However, the affinity between arsenic and the gel can be predicted in terms of a dimensionless separation factor [103], R_L, defined by Eq. 7:

$$R_L = \frac{1}{1 + bC_{in}} \tag{7}$$

where C_{in} is the initial arsenic concentration (mg/l) and b is the Langmuir parameter. Values of R_L<1 represent favorable adsorption and values of R_L>1 represent unfavorable adsorption. Affinity between arsenic and Zr(IV)-loaded SOW gel are checked and it was found that the values of R_L (shown in Fig. 5.12), calculated for the

adsorption of As(III) and As(V), were within 0 and 1, which indicates a highly favorable adsorption.

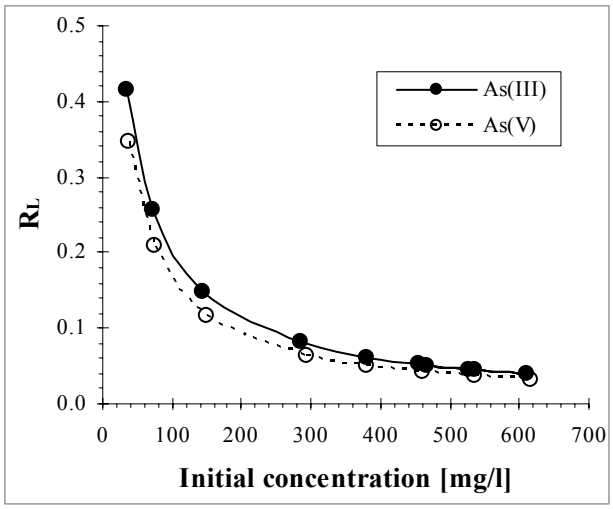


Fig. 5.12. Separation factor of As(III and V) adsorbed on the Zr(IV)-loaded SOW gel. Conditions: S/L ratio= 1.67 mg/ml, *t*= 24 h, *T*= 30ºC, pH= 3 (As(V)), 10 (As(III)).

Table 5.2. Comparison of maximum sorption capacity with other adsorbents.

Adsorbent	*q* (mg/g)	Species	Reference
La(III)-loaded orange waste	43	As(V)	Present study
Ce(III)-loaded orange waste	43	As(V)	Present study
Zr(IV)-loaded orange waste	88	As(V)	Present study
La(III)-impregnated alumina	12.88	As(V)	[80]
Activated carbon	1.05	As(V)	[104]
Ce(IV)-doped iron oxide	16.00	As(V)	[105]
Lessonia nigrescens, an algae	28.20	As(V)	[106]
La(III)-loaded orange waste	42	As(III)	Present study
Ce(III)-loaded orange waste	42	As(III)	Present study
Zr(IV)-loaded orange waste	130	As(III)	Present study
Iron oxide-coated sand	0.029	As(III)	[13]
Polymetallic sea nodule	0.74	As(III)	[107]
Iron oxide coated cement	0.69	As(III)	[108]
Sorghum biomass	3.6	Total As	[109]

5.9. COLUMN ADSORPTION AND ELUTION TESTS

The performances of the La(III)- and Zr(IV)-loaded SOW gels in continuous operation for the removal of As(V) and As(III) were studied using a packed column. Figure 5.13(a) shows the individual breakthrough profile of As(V) and As(III) with La(III)-loaded SOW gel where the feed concentration for both As(V) and As(III) was maintained at 10 mg/l, while Fig. 5.13(b) shows the same with the Zr(IV)-loaded SOW gel at a feed concentration of 15 mg/l. From Fig. 5.13(a), it is seen that the breakthrough for As(V) and As(III) occurred at 120 and 100 bed volumes (BV), respectively, indicating that As(V) and As(III) can be completely retained on the gel up to these mentioned bed volumes, while complete saturation was achieved consequently at 690 and 280 BV. Here, bed volume (BV) represents the volume ratio of the solution passed through the column to that of the packed gel. On the other hand, Fig. 5.13(b) shows a higher breakthrough point for both As(V) and As(III) indicating a higher adsorption capacity of Zr(IV)-loaded SOW gel compared to that of La(III)-loaded SOW gel. However, before reaching the complete saturation of the bed, the pH of the effluent, in all cases, increased slightly, which conforms to that of batch-mode adsorption. Once the bed is completely saturated, there was no change in pH. The adsorption capacities calculated from the breakthrough profiles were 14.2 mg-As(V)/g and 10.5 mg-As(III)/g for La(III)-loaded SOW gel while that for Zr(IV)-loaded SOW gel were 36.27 mg/g and 35.12 mg/g for As(V) and As(III), respectively. The effective adsorption capacities thus calculated were less than the corresponding equilibrium sorption capacities, which may be attributable to various phenomena such as channeling and too short contact time between the gel and the arsenic solution to allow equilibrium to be attained in the column. Similar results have also been reported by Lenoble et al. [3] for arsenic removal on MnO_2-loaded resin and by Zouboulis and Katsoyiannis [48] for arsenic removal using iron oxide loaded alginate beads.

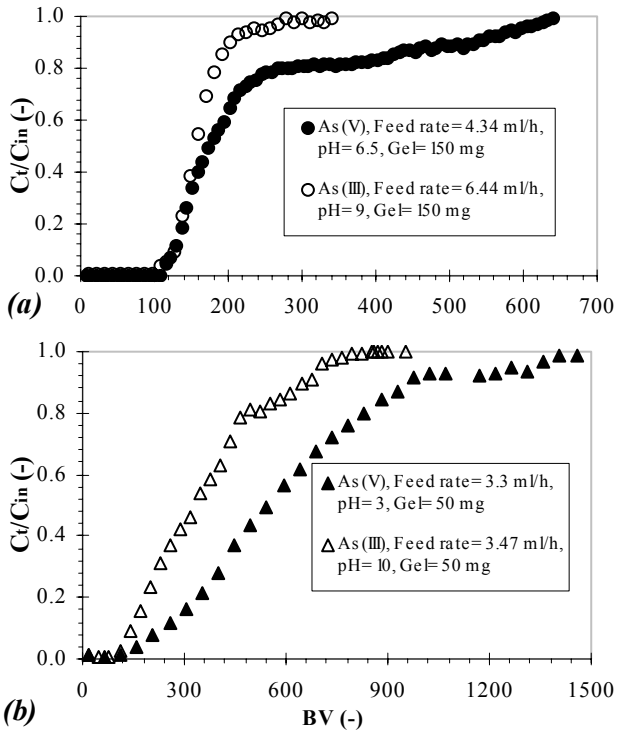


Fig. 5.13. Column adsorption tests arsenic adsorption onto (a) La(III)-loaded SOW gel and (b) Zr(IV)-loaded SOW gel where C_t and C_{in} denote the adsorbate concentration in the effluent at time t and the initial concentration.

Empty bed contact time (EBCT) is a very useful parameter for designing a column. EBCT is defined by the following equation (Eq. 8) [110]:

$$\text{Empty Bed Contact Time (EBCT)} = \frac{V}{Q} \tag{8}$$

where V and Q are stationary phase volume and mobile phase flow rate, respectively. In this work EBCT was measured for arsenic removal using the La(III)-loaded SOW gel in column-mode, which was 8.3 and 5.6 min for As(V) and As(III), respectively. The obtained results resemble to that of AdEdge Technologies, Inc. (Atlanta based company) who has used a resin (commercial name: ID-33) to remove arsenic since 1999 [111]. Similarly, EBCT for the column operated with the Zr(IV)-loaded SOW gel was calculated as 4.7 and 4.3 min for As(V) and As(III), respectively.

After complete saturation of the bed, packed with the La(III)-loaded SOW gel, elution tests were carried out using 1 M HCl for As(V) and 1 M NaOH for As(III) (Fig. 5.14 (a)), which shows that more than 20 fold enrichment was attained for As(V),

while the preconcentration for As(III) was less than 4 fold. These results are in agreement with those reported by Chanda et al. [112,113] for arsenate and arsenite adsorption on chelating resins. The elution of As(V) in the present study was very efficient since more than 95% of the adsorbed arsenic was eluted within less than 5 h by using less than 25 ml of eluent while that of As(III) took a fairly long time (longer than 20 h). La(III) was not detected in the effluent during elution of arsenite, while during elution of arsenate, it was eluted together with the arsenate, suggesting that it is necessary to load the metal again onto the gel for the next operation.

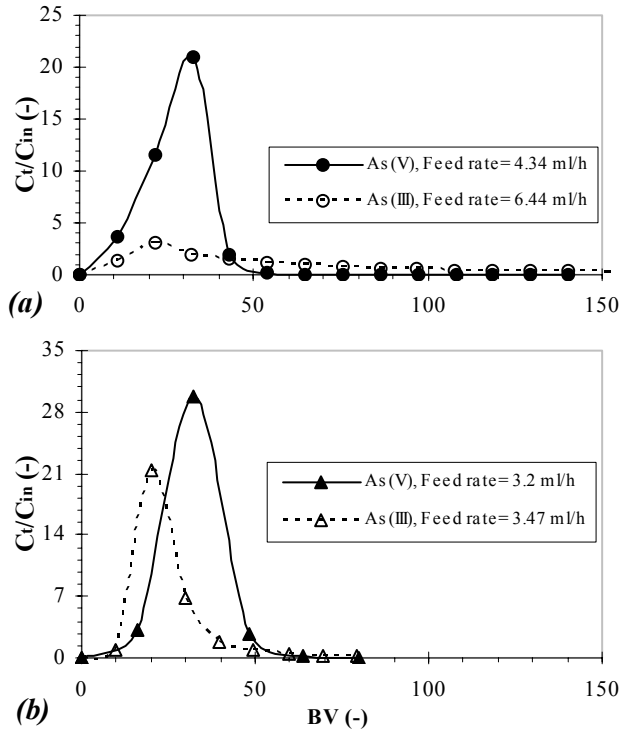


Fig. 5.14. Elution profiles of arsenic onto (a) La(III)-loaded SOW gel and (b) Zr(IV)-loaded SOW gel.

Figure 5.14(b), on the other hand, shows the elution behavior of As(V) and As(III) from the Zr(IV)-loaded SOW gel using 1 M NaOH. About 30 and 20 fold enrichment was attained for As(V) and As(III), respectively. The elution was found to be very efficient since 95% and 96% of the adsorbed As(V) and As(III), respectively, was eluted. Moreover, leakage of the loaded zirconium was very insignificant during the elution processes contrary to the case of Fe(III)-loaded crosslinked pectic acid gel

[114] and La(III)-loaded SOW gels [115]. In addition to that, the gel was tested for up to six adsorption-elution cycles for As(V) in column-mode and it was found that the gel can be efficiently used without any damage (Fig. 5.15). Comparison of the amount of As(V) adsorbed and eluted in each cycle verified that As(V) could be quantitatively recovered under continuous flow systems. Such preliminary experiments demonstrated that the gel was compatible with column operation where regeneration is also possible.

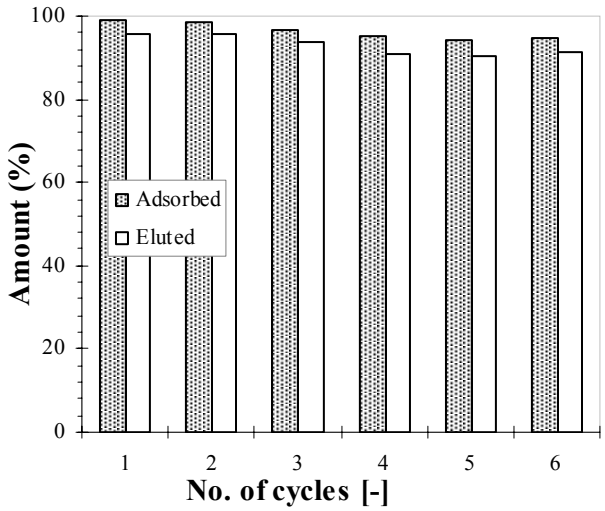


Fig. 5.15. Adsorption-elution profiles of As(V) onto Zr(IV)-loaded SOW gel at pH 3. Conditions: eluting reagent = 1 M NaOH, feed rate = 4.6 ml/h, feed concentration = 15 mg/l.

Chapter 6

Conclusion

The present study clearly establishes that all the gels (La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels) prepared are effective adsorbents for arsenic over a wide range of pH. The adsorption capacities were also remarkably high. However, among the three gels tested, the Zr(IV)-loaded SOW gel exhibited the highest sorption capacity. The arsenic adsorption system was found to be uninterrupted with the presence of chloride, carbonate and sulfate anions. But phosphate, on the other hand, interrupted arsenic adsorption. Kinetic studies, conducted with the La(III)- and Zr(IV)-loaded SOW gels, suggested that the system might follow pseudo-second-order reaction.

Although the sorption mechanism is tough to understand because of the complex nature of the orange waste, ligand substitution is supposed to be the main exchange reaction which happens between hydroxyl ions or water molecules and arsenic anions. However, column-mode adsorption for arsenic was also tested by using the La(III)- and Zr(IV)-loaded SOW gels and found to give encouraging results. The Zr(IV)-loaded SOW gel was tested for its repeated use and was found to be efficient without any damage.

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arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, J. Colloid Interface Sci. 310 (2007) 57-73.

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Part II

Removal and recovery of phosphorus from water and wastewater by means of adsorption onto metal-loaded saponified orange waste gels

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Chapter 7

Introduction

7.1. INTRODUCTION

As population increases, the quantity and quality of water resources have become the focus of many debates and studies. Wastewater or contaminated water is a big environmental problem all over the world. Limiting runoff and leaching of nutrients supplied for plant nutrition is a major concern of policymakers pushing for clean water resources and an overall sustainable system. Impacts of excess phosphorus, a limiting nutrient, on water quality have been well documented [1-3]. Simple solutions to prevent pollution have been difficult to come by because the chemistry and flow pathways of phosphorus cause strategies to manage phosphorus.

Phosphorus is an essential nutrient for growth of organisms in most ecosystems. It is a very important material for many industries as well. The extensive industrial use of phosphates inevitably results in large amounts of phosphate-bearing wastes, which are usually discharged into municipal and industrial water effluent streams. Water, on the other hand, is an important resource in every human society and is used in homes for drinking, cooking, washing, heating and in industry for various purposes. It is equally important in the field of agriculture too where it is used for irrigation of crops. The result of using water is the generation of wastewater, which is normally collected by a sewage system and channeled to the wastewater treatment plant where after it is returned to the natural eco-system by discharging into waterways.

Phosphate discharged into surface waters can disturb the balance of organisms present in water and affect water quality, mainly through the depletion of the dissolved oxygen level as the algae decay. Depletion of the oxygen level in confined water bodies e.g. bays, lakes and ponds causes eutrophication [4], which, in turn, has a harmful effect on fish and other aquatic life, resulting in a reduction in biodiversity as well as unfavorable human environmental health. In order to control and remedy such problems and to maintain a sustainable green environment for the forthcoming

generation, it is desirable that water treatment facilities remove phosphorus from the wastewater before it is returned to the environment. On the other hand, experts agree that there is no foreseeable increase of phosphate resources, which are considered to be limited. At the same time there have been some alarming reports that deposits of high-grade phosphate ores are likely to be depleted in the next few decades [5,6]. Thus, it is very important to develop a recovery process for phosphates from phosphate-containing wastewater as an alternative source of phosphates to compensate for such global exhaustion of high grade phosphate ores. In order to have a safer aquatic world, many directives have been made which include meeting a global phosphate discharge limit of 0.5-1.0 mg/l [7]. This calls for better wastewater technologies and more research is still being undertaken in this field throughout the world.

7.2. UNDERSTANDING OF PHOSPHORUS REMOVAL PROCESSES

Phosphorus removal methods from wastewater including chemical precipitation, crystallization including MAP (magnesium ammonium phoshate) and HAP (hydroxyapatite) processes, adsorption, and biological methods have been extensively studied during past decades. More effective for phosphate removal is chemical treatment, which is still subjected to costs and problems of sludge handling, its disposal and neutralization of effluent [8]. Neutralization of effluent not only increases the chemicals expenditure but also is detrimental to biological treatment process. Nevertheless, biological removal of phosphates in bioreactors is performed by microorganisms. The species commonly used are non-specific and environmentally enriched from the sludge by the incubation conditions. Several attempts to intentionally use specific microorganisms as cleaning agents were reported [9,10]. However, the removal efficiency of phosphates in biological treatment plant usually does not exceed 30%, which means that remaining phosphate should be removed by another technique [11]. Presently, there has been a trend towards combining biological and chemical phosphorus removal method to achieve better result. Anion exchangers are also very commonly used but they have various shortcomings such as low selectivity in the presence of other competing anions [12]. Generally activated alumina treated by aluminum sulfate, zirconium ferrite and

chelating resins is considered to be most practical but these are too costly for wastewater treatment [13].

When considering what method is more effective for removing phosphorus in wastewater, apart from measuring effluent concentrations, other factors are also important. Sludge handling and disposal are some of such issues which have been much debated today. In the past, sludge was directly used as fertilizer on arable land, but this has now been almost totally stopped because of fear of spillage of hazardous materials [14,15]. A good comparison of which method is more effective must also consider the extra cost of treating sludge produced during operation. Considering such issues alternative removal technologies have been investigated by many scientists and researchers who have prevailed adsorptive removal of phosphate from aqueous solution. Such research finding is, however, encouraging to establish, evaluate and present a treatment method for removing phosphate using cost-effective adsorbent.

Adsorption is one of the techniques that would be comparatively more useful and economical for phosphates removal. In adsorption, the separation mechanism involves attracting one or more solutes in a liquid or gas mixing to the surface of a solid adsorbent where they are held by intermolecular forces [16,17]. Nevertheless, increasing attention has been paid to adsorptive removal of phosphate from aqueous solutions. Apart from the conventional adsorbents such as activated carbon [18] and alumina [19], the application of low cost and easily available materials in wastewater treatment has been studied in recent years, which include biomaterials, algae, seaweed, waste materials and by-products, humic substances etc.

Adsorbents based on biomaterials, often called biosorbents, have been studied as a cost-effective and environmentally-benign means to remove pollutants. Chemically treated aspen wood particles [20] were found to be effective in removing phosphate from solutions. Microalgae immobilization in polymeric matrices has also become an attractive alternative that facilitates the biomass recovering and provides a greater operational flexibility [21]. Moreover, immobilized-microalgae system prevents biomass from being washed out. Chitosan immobilized *Scenedesmus* was investigated for its adsorption behavior and reported to be effective for phosphate removal [22,23]. Collagen fiber, an abundant natural biomass, comes from the skin of domestic animals and traditionally is used as a raw material of leather manufacturing. It is water

insoluble but is a hydrophilic material. Fe(III) and Zr(IV)-loaded collagen fiber was tested for removing phosphate from aqueous solution and its adsorption behavior was reported [24]. Beside this, many other low-cost adsorbents have been so far investigated for phosphate removal from aqueous solutions, which include banana stem [25], coir pith carbon [26], surface modified coir pith [27], Fly ash [28.29], blast furnace slags [30,31] etc.

7.3. ORANGE WASTE AND ITS TRANSFORMATION TO ADSORPTION GEL

The bio-waste material investigated in this study is an agricultural waste generated in orange juice factories. Orange waste, particularly peel, contains around 10% pectin which exists in the cell wall as an intercellular cementing material. Pectin is a polysaccharide in which pectic acid, an acidic polysaccharide, is partly esterified by methyl groups. It is easily converted into pectic acid by saponification with alkalis such as calcium hydroxide [32]. Once the gel is prepared from orange waste, it exhibited good adsorption behavior for phosphate [33,34] by loading with metal ions e.g. lanthanum, cerium and zirconium. In relation to the adsorptive removal of arsenic, phosphate and fluoride [35-37] by metal loaded cation exchange resins, it has been reported that not only the loaded metal ion but also the polymer matrices of the resins greatly affect their adsorption behavior. Consequently, it is necessary to investigate the role of orange waste gel as the carrier of the loaded metal ion. To reach this goal, the prepared gel was loaded with La(III), Ce(III) and Zr(IV) ions and investigated their sorption capacity, pH dependence, kinetic behavior in the view of phosphate adsorption from an aquatic environment.

7.4. RESEARCH OBJECTIVES

This work is a part of comprehensive study on removal of hazardous anions from aquatic environment by using chemically modified orange waste. The main objective of this study is to remove phosphorus from synthetic solution as well as industrial wastewater. Moreover a comparison of phosphate removal efficiency with commercially available adsorbents (Zirconium ferrite and MUROMAC XMC 3614) will be made. The objectives of this research are summarized as follows:

- To investigate the role of orange waste as an adsorbent to remove phosphate from synthetic wastewater and industrial effluent that contains phosphorus.
- To determine the adsorption behavior and to estimate the maximum adsorption capacity of the gel to phosphorus.
- To study the kinetic behavior, pH dependence, effect of the presence of other common anions and to analyze the data.
- To compare sorption capacity of the prepared gel with zirconium ferrite and Zr(IV)-loaded MUROMAC XMC 3614, two common adsorbents employed for removal of phosphate.
- To establish the orange waste as a useful agricultural by-product in the form of adsorption gel.
- To contribute to the protection of environment and to lead towards sustainability.

Chapter 8

Research Background and Literature Review

8.1. SOURCES OF PHOSPHORUS

Phosphorus is an important element, making a major contribution to agricultural and industrial development. The origin of all inorganic phosphorus is the class of mineral known as apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), which is a group of phosphate minerals, usually referring to hydorxylapatite, fluorapatite and chlorapatite, named for high concentrations of OH^-, F^- and Cl^- ions, respectively, in the crystal. Average content of phosphorus pentoxide (P_2O_5), suitable for phosphoric acid and elemental phosphorus, in rock phosphate is counted to be approximately 40% [38]. A weighted world average phosphorus concentration for rock phosphate is estimated to be 144 mg/g [39].

8.2. PHOSPHORUS IN WATER AND WASTEWATER

The major sources of phosphorus in water and raw wastewater are derived from human, domestic and industrial wastes as well as run-off from phosphorus-rich fertilized land. All living creature contain phosphorus in one form or other. Each person contributes about 2-3 g of phosphorus to wastewater each day [40]. Most of this phosphorus gets into wastewater from human waste. Another important source of phosphorus contamination is detergents, which make up about a third of daily contribution. However, with the prohibition of phosphorus based detergents in most countries, input from this source is limited. Besides, there are natural processes which take a key role for spreading phosphorus in the aqueous environment. Spreading of phosphorus via natural as well as anthropogenic processes is discussed here in after.

8.2.1. Natural processes

During the natural process of weathering, the rocks gradually release the phosphorus as phosphate ions which are soluble in water and thus mineralize

phosphate compounds breakdown. Phosphates (PO_4^{3-}), which are formed from elemental phosphorus, exist mainly in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate where each compound contains phosphorous in a different chemical arrangement. However, apart from weathering of rock phosphate, there are many other natural processes through which phosphorus can enter into the aquatic environment. These processes are discussed hereinafter.

8.2.1.1. Precipitation

Rain and snow scour the air, accumulating airborne phosphorus (orthophosphate and particulate forms) and other pollutants, which are deposited in the watershed. Concentrations in precipitation generally range from 0.02 to 0.04 mg-P/l [41].

8.2.1.2. Atmospheric fallout (Dry fall)

Wind currents deposit phosphorus and other pollutants attached to sediment carried from other areas. The total loading from dry fall can be in the same order as precipitation.

8.2.1.3. Decomposition of organic materials

Plants, atmospheric fallout, liquid and solid wastes are accumulated in urban areas. All these wastes are decomposed, producing phosphates (typically in organic form).

8.2.1.4. Erosion

It is well recognized that the origin of all inorganic orthophosphate is the class of minerals known as apatite. Since phosphorus moves through the system toward the reservoir or aquifers, the concentration of phosphorus increases, a phenomenon known as pollutant enrichment. So the erosion of watershed soils may cause increase in phosphate in aqueous environment.

8.2.2. Anthropogenic processes

In addition to the natural sources of nutrients, phosphorus enters the environment from a number of anthropogenic sources. These are considered below.

8.2.2.1. Commercial fertilizer

Commercial fertilizers typically contain some form of phosphates (P_2O_5). Runoff from intensively farmed land often contains high concentrations of inorganic fertilizer. Phosphate applied to farmland may spread to the wider environment by:

- drainage water percolating through the soil and eventually leaching soluble plant nutrients;
- washing of excreta, applied to the land as fertilizer, into watercourses; and
- the erosion of surface soils or the movement of fine soil particles into subsoil drainage systems.

8.2.2.2. Domestic detergents

Domestic detergents are a major source of phosphorus in sewage effluents. Phosphates are used as a builder in washing powders to enhance the efficiency of surfactants by removing calcium and magnesium to make the water "soft". In 1992, approximately 845,600 tonnes of detergent of various types was used by the UK, all of which have different effects on the environment [42]. However, the scenario has been changed a little because most detergent products are now phosphate free.

8.2.2.3. Animal manure

Manure of animals is also another source from where phosphate can enter to the environment. Wastes from horse, cattle, sheep, and pet and wild animals that are exposed to storm water can produce organic phosphates.

8.2.2.4. Automotive products

Hydraulic fluids, fuels, tires and rubber compounds contain phosphorus. Once these materials deposited on impervious surfaces, storm water washes into drainage to increase phosphorus content.

8.3. IMPORTANCE OF PHOSPHORUS

Phosphorus is one of the key elements necessary for growth of plants and animals. In lake ecosystems it tends to be the growth limiting nutrient. Moreover, it is the backbone of DNA. Phosphates are not toxic to people or animals unless they are

present in very high levels. It acts as a crucial part of life and health because this mineral element is essential to the structure and function of much of the body. Phosphorus is the best known as a nutrient for its part in the creation of bones and teeth. Besides, phosphorus has an extensive industrial application in different fields e.g. electroless plating, surfactants, cleansers, water treatment, fertilizer, pesticides, lubricant and so forth.

8.4. PHOSPHORUS COMPOUNDS IN AQUEOUS SOLUTION

Phosphates in raw and domestic wastewater usually occur in dissolved form. The distribution of P species among environmental compartments (e.g. between water and sediments), significantly affects the bioavailability of these species to various organisms. In aqueous solutions phosphorus is usually found in three forms such as organic phosphates (with –P-O-C- bonds), condensed inorganic phosphates (with -P-O-P bonds) and inorganic orthophosphates (PO_4^{3-}). The speciation and corresponding pK_a values [43] are shown in Table 8.1.

Table 8.1. Dissociation constants of phosphate.

Species	Equations	pK_a
Phosphate	$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$	2.12
	$H_2PO_4^- \leftrightarrow H^+ + HO_4^{2-}$	7.21
	$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	12.67

However, the distribution of phosphate varies significantly depending on the pH. Among other factors, temperature, redox conditions affect the release and uptake of P. The speciation of phosphate with respect to pH based on their dissociation constants is depicted in Fig. 8.1, which shows that P has almost completely dissociated and presented in the form of monovalent, divalent and trivalent anions [44].

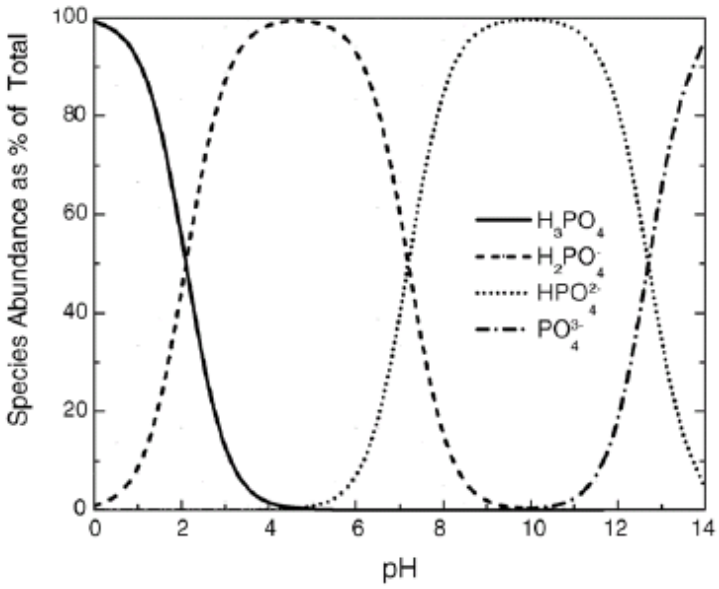


Fig. 8.1. Species as a percentage of the total concentration of phosphate.

8.5. PHOSPHORUS RELATED ENVIRONMENTAL THREATS

There are several environmental hazards due to the excessive presence of phosphate. The eutrophication of lakes and waterways is an international environmental problem caused by the nutrient e.g. phosphorus and nitrogen. Algal growth is known to be promoted by the discharge of such nutrients. The over fertilization of water bodies results in algal blooms which apart from aesthetic disturbances and odors, may also cause serious environmental hazards. Recently, the off coast sea water of Kollam and Trivandrum districts (Kerala, India) were covered with red bloom algae, which seriously affected the lives of fishermen in close proximity of the affected area due to the death of tones of fishes [45]. Algal bloom, which results high economic damage in coastal oceans, can be caused by phosphate run-off episode. This eventually leads eutrophication to happen. However, a simple diagram for occurrence of eutrophication [46] is presented in Fig. 8.2. Phosphorus in water can give rise of plant matter (algae), which become over crowded and die resulting a great deal of oxygen to break down. The oxygen is also consumed partly through the oxidation of carbon into carbon dioxide and partly through the oxidation of nitrogen into nitrate. The use of oxygen in this way results in oxygen shortages for aquatic animals such as fish, which eventually die. Though nitrogen is regarded as the

main contributor to eutrophication in seawater, phosphorus is still considered the dominant factor in lakes and stagnant waterways [47].

Red tide is another environmental problem that is common in the gulf of Mexico and along some Asiatic and European coastlines as well as Florida waters. It is a colloquial term used to refer to a natural phenomenon known as harmful algal bloom (HAB). This type of bloom is caused by algal species known as *Karenia brevis*, and these blooms occur almost annually along Florida waters. The density of these species during a bloom can exceed tens of millions of cells per liter of seawater, and often discolor the water a deep reddish-brown hue where the name is derived from [48]. The red tide phenomenon occurs where large rivers discharge nutrients into the sea. Nutrient, especially phosphorus, is known to be the cause of this problem.

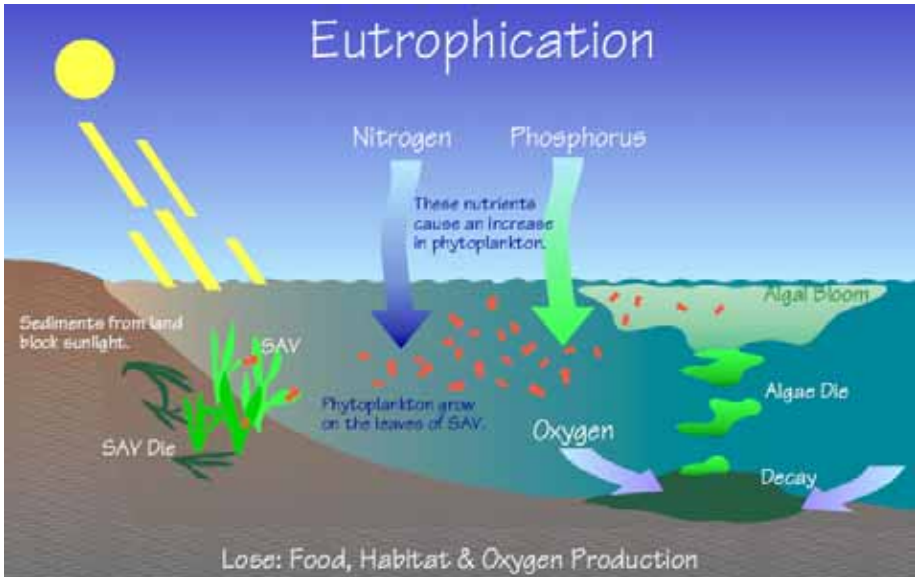


Fig. 8.2. Cause and effect of eutrophication.

Even though many initiatives have been taken to solve the problem and one of the major advances in this area is the banning of phosphorus based detergents in many countries, the removal of phosphorus in wastewater has to be improved to minimize the environmental problems.

8.6. PHOSPHORUS REMOVAL METHODS

Development of technologies for phosphorus removal started in the 1950s in response to the issue of eutrophication and the need to reduce the levels of phosphorus entering surface waters [49]. Removal was initially achieved by chemical

precipitation, which remains the leading technology today. Even though, biological phosphorus removal has become firmly established, crystallization technology has also completed its progress towards commercialization. Adsorption technology has been investigated very recently and its development is at advanced stage.

8.6.1. Chemical precipitation

Chemical precipitation is in essence a physico-chemical process, comprising the addition of a divalent or trivalent metal salt to wastewater, causing precipitation of an insoluble metal phosphate that is settled out by sedimentation. The widespread use of chemical precipitation for phosphorus removal in wastewater treatment started in Switzerland during the 1950s, in response to the growing problem of eutrophication. However, the most suitable metals are iron and aluminum, added as chloride or sulfates. Lime may also be used to precipitate calcium phosphate. Chemical precipitation is a flexible approach to phosphorus removal and can be applied at several stages during wastewater treatment. The process has been classified as primary, secondary and tertiary precipitation depending on the stages of dosing chemicals. Tertiary treatment, however, is not generally favored because of high chemical costs and the creation of an additional sludge.

Chemical precipitation typically produces phosphorus bound as a metal salt within the wasted sludge. When disposed to agriculture, it therefore has potential value, although research on bioavailability is inconclusive [50]. Moreover, it is not easy to control optimum dosing conditions. Such uncertainties have contributed to the desire to develop alternative technologies that potentially offer a more valuable and consistent product for recycling phosphorus to agriculture and industry.

8.6.2. Biological phosphorus removal

In the late 1950s, the development of biological phosphorus removal was established and it was found that under certain conditions, activated sludge could take up a considerable amount of phosphorus [51,52]. Based on this phenomenon, know as “luxury uptake”, a number of applications and processes have been developed and the technology is now firmly established. Activated sludge plants operated to achieve biological phosphorus removal require an anaerobic zone prior to the aerobic zone

and need to be operated in a plug-flow manner. Under anaerobic conditions phosphates are released form the biological sludge into solution while subsequent aeration induces the sludge to take up phosphates from the solution in excess of normal metabolic requirements. Wastewater treatment plants operated in this manner are capable of removing 80% to 90% of influent phosphorus and producing an effluent phosphorus concentration <1 ppm [53]. However, the biological phosphorus removal technology has the advantage of avoiding the use of chemicals and excess sludge production. Additionally, it requires more complex plant configurations and operating regimes [54].

8.6.3. Crystallization technology

It is possible to remove phosphate from aqueous solution as hydroxylapatite (HAP) by crystallization reaction with calcium ion when seed crystalline substance coexists in the solution. The development of crystallization technology started in the 1970s, in response to more stringent phosphorus removal requirements combined with the desire to produce a more marketable end-product. This technology is based on the crystal nucleation and growth chemistry. Although there have been a number of initiatives taken throughout the world, the leaders in this technology are DHV Consulting Engineers, who adapted their expertise in water softening [55]. This is a process, which is based on the crystallization of calcium phosphate on a seeding grain, typically sand, within a fluidized bed reactor. Process conditions are adjusted to promote calcium phosphate crystallization by adding either caustic soda or milk of lime. The high rate of crystallization allows a short retention time and therefore a small reactor. Pellets are periodically removed and replaced by smaller diameter seed grains. This allows continuous operation and ensures good fluidization.

8.6.4. Ion exchange

Ion exchange process has also been investigated for phosphate removal from aqueous medium. In this process, ammonia and phosphate ions are removed from tertiary wastewater to produce struvite, which is an ammonium magnesium phosphate mineral ($(NH_4)MgPO_4 \cdot 6H_2O$). A demonstration of ion exchange process for removal of ammonium phosphate from sewage has been reported to be built in Italy [56,57].

The process uses a cationic resin to remove the ammonium ions and a basic resin to remove phosphate ions. Regeneration releases the ammonium and phosphate that are precipitated as struvite. Though ion exchangers are generally used, they have low selectivity in the presence of other competing anions.

8.6.5. Magnetic separation of phosphorus

Magnetic separation of phosphorus, examined in the 1970s [58], was said to be very promising as the effluent values (0.1-0.5 mg-P/l) can be achieved at a costs comparable with other processes [59]. Magnetic water treatment systems are essentially a tertiary treatment, where lime is used to precipitate calcium phosphate attached to magnetite and separated using an induced magnetic field. Following isolation, the magnetite is uncoupled from the phosphate in a separator unit by shear forces and a drum separator. The separated suspension of calcium phosphate or carbonate in water is then further processed depending on final product use. This process is advantageous considering high elimination performance, compact process and low power input.

8.6.6. Adsorption of phosphorus

In developing countries, industries can not afford to use conventional wastewater treatment chemicals like alum, ferric chloride, and polymer flocculants because of their high price. So for economic feasibility, an inexpensive and easily available adsorbent is of high priority for removing hazardous pollutants form aqueous medium. Adsorption is one of the techniques, which is comparatively more useful and economic for phosphate removal [60]. Removal of phosphate from aqueous solution by means of adsorption has been investigated in recent years by using various sorbents, which include bioadsorbents e.g. wood particles [20], microalgae e.g. *Scenedesmus* [22,23], seaweed e.g. carrageenan [61] and waste materials or by-products e.g. coir pith carbon [26], fly ash [29], blast furnace slags [30,31] etc. The potential advantages are that no additional sludge is produced, reagents are not needed to overcome high alkalinity and wastewater pH is unaffected. However, the viability of phosphate adsoption process is dependent on the development of adsorptive materials.

Chapter 9

Experimental

9.1. ADSORBATE AND OTHER METAL SOLUTIONS

A phosphate stock solution (1000 mg/l) was prepared from phosphoric acid dissolved in deionized water. The stock solution was further diluted in order to prepare working solutions of required concentrations. Aqueous solutions of lanthanum(III), cerium(III) and zirconium(IV) were prepared by dissolving corresponding analytical grade metal chlorides or nitrates in 0.1 M hydrochloric acid. If required, 0.1 M *n*-2-hydroxyethylpiperazine-*n*-2-ethanesulphonic acid (HEPES), the buffering agent, was mixed at arbitrary volume ratio. Working solutions of phosphite and hypophosphite were prepared from sodium phosphite dibasic pentahydrate ($Na_2HPO_3 \cdot 5H_2O$) and sodium hypophosphite monohydrate ($Na_2PH_2O_2 \cdot H_2O$), respectively.

9.2. PREPARATION OF SOW GEL AND LOADING WITH METAL IONS

The preparation of saponified orange waste gel as well as loading with metal ions e.g. lanthanum(III), cerium(III) and zirconium (IV) has been discussed earlier in Section 4.2.

9.3. KINETIC STUDIES

Kinetic studies of phosphate adsorption onto the La(III)-, Ce(III), and Zr(IV)-loaded SOW gels were carried out individually to asses the equilibration time for adsorption and to have idea about the kinetic behavior e.g. adsorption rate. However, 25 mg of metal-loaded gel was put into each of thirteen 50 ml conical flask together with 15 ml of phosphate working solution. In case of the La(III)- and Ce(III)-loaded SOW gels, the initial concentrations of phosphate working solution was taken as 20 and 40 mg/l. The pH for both initial solutions were adjusted at 7.5 by adding a small amount of NaOH or HCl. Kinetics of phosphate adsorption onto the Zr(IV)-loaded

SOW gel, on the other hand, was tested by taking 20, 100, 260 mg-P/l each of which was maintained at pH 3 (optimum pH). The flasks were then shaken in a thermostatic shaker (THOMAS thermostatic shaking incubator AT24R) maintained at 30ºC at 140 rpm. Phosphate concentration was measured at 13 different contact times (0, 5, 10, 15, 30, 60, 120, 240, 480, 600, 900, 1200 and 1440 min). At the end of each contact time, the suspension was immediately filtered through a 1 μm filter paper and the filtrate was analyzed. The amount of phosphate adsorbed at time *t* was calculated from the mass balance between initial concentration and concentration at time *t* to analyze the adsorption rates of phosphate onto different metal-loaded gels.

9.4. BATCH-MODE ADSORPTION EXPERIMENTS

Batch-wise adsorption tests for phosphate were carried out to examine the adsorption behavior of phosphate onto the La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels, and zirconium ferrite as well as the Zr(IV)-loaded MUROMAC XMC 3614 resin. The later two adsorbents were tested to compare the sorption capacities. However, phosphate adsorption as a function of pH was first examined in a series of adsorption tests where the initial phosphate concentration was maintained constant at varying pH and thus the optimum pH for adsorption was determined. Here pH was adjusted by adding small amount of NaOH or HCl. All these batch adsorption tests were carried out in 50 ml conical flasks by shaking 25 mg (dry weight) of adsorbents together with 15 ml of phosphate solution at 140 rpm using a thermostated shaker maintained at 30ºC for 24 h to attain equilibrium, after which the suspensions were filtered through a 1 μm filter paper and their equilibrium concentrations were measured. The quantity of adsorbed phosphate was calculated from the decrease in phosphate concentration.

Adsorption tests to obtain an adsorption isotherm were carried out at optimum pH as well as at neutral pH. Reproducibility of all these batch adsorption tests as well as column-mode experiments, which will be described in Section 9.5, was tested in triplicate and the mean values were taken.

9.5. COLUMN-MODE ADSORPTION AND ELUTION TESTS

The continuous adsorption tests for phosphate removal were carried out individually by using the La(III)- and Zr(IV)-loaded SOW gels. These tests were

carried out by using transparent glass columns as described earlier in Fig. 4.2. Approximately 150 mg gel was first soaked in deionized water to facilitate swelling and then packed into the column. The volume of the packed gel was calculated to be 0.60 cm^3. The test solution, containing 20 mg-P/l at pH 7.5 (for La(III)-loaded gel) and at pH 3 as well as pH 7 (for Zr(IV)-loaded gel) were passed through the column. However, either an EYELA model MP-3N Micro Tube Pump or an IWAKI model PST-100N peristaltic pump was used to percolate the phosphate solution. Prior to the start of the dynamic studies, the column was conditioned by passing water at the same pH for 24 h. A fraction collector (BIORAD Model 2110) was used to collect the fractions of effluent at definite intervals of time in 8 ml plastic tubes for the measurement of the arsenic concentration.

After complete adsorption, an elution test was carried out using 0.4 M HCl solution and 0.2 M NaOH for La(III)-loaded SOW gel and Zr(IV)-loaded SOW gel, respectively. However, the column was washed with de-ionized water before carrying out elution tests. The eluted phosphate concentration was analyzed as before.

Chapter 10

Results and Discussion

10.1. KINETIC STUDIES

Kinetics of phosphate adsorption onto La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels were studied with the variation of phosphate concentration and time. Figure 10.1 (a) shows the rate of phosphate uptake by the La(III)- and Ce(III)-loaded SOW gels. The equilibrium in all cases was found to be attained in 15 h. However, 24 h was taken as the equilibrium time for subsequent adsorption tests. In every case, phosphate uptake was directly proportional to higher initial concentration. This may be attributed to the development of a high concentration gradient between the bulk and adsorbed phases. Figure 10.1 (a) shows that the initial phosphate adsorption is very fast. The initial rapid step may be attributed to diffusion controlled sorption of phosphate onto gels [62]. Similar behavior has also been observed for phosphate adsorption on δ–MnO_2 [63] and on ion exchange fibers [64]. Figure 10.1 (a) also shows that the phosphate adsorption curves become asymptotic to the time axis signifying that no noticeable incremental change is taking place over time. It can also be seen that there is no obvious difference in kinetic behavior between the La(III)- and Ce(III)-loaded SOW gels under the experimental conditions. However, uptake of phosphate (20, 100, 260 mg-P/l) with time by using the Zr(IV)-loaded SOW gel has been depicted in Fig. 10.1(b) where it is shown that the initial phosphate adsorption is rapid which gradually slows down and reaches equilibrium. Similar to the case of the La(III)- and Ce(III)-loaded SOW gel, 24 h was taken to happen the equilibrium adsorption between solute and adsorbent (Zr(IV)-loaded SOW gel).

The results described in Figs. 10.1 (a) and (b) can be interpreted according to pseudo-second-order rate equation with a coefficient of determination of no less than 0.99. Since nonlinear regression analysis software packages can be used for the direct determination of model parameters and is supposed to give a more accurate determination of model parameters than linearization methods [65], a statistical

software package (XLSTAT) has been used to determine the kinetic parameters of this study. However, the values of kinetic parameters obtained from nonlinear regression were found to be similar in magnitude to that of linear regression analysis (Table 10.1).

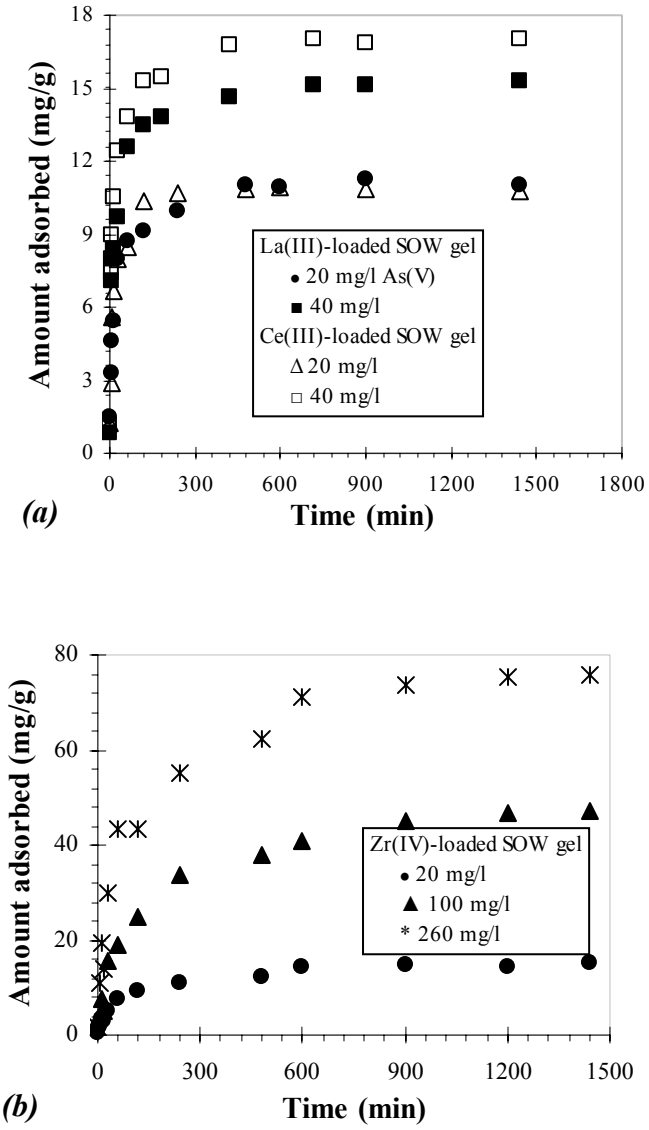


Fig. 10.1. Effect of shaking time and initial phosphate concentration: (a) La(III)- and Ce(III)-loaded SOW gels and (b) Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, T = 30°C.

Table 10.1. Kinetic parameters for the adsorption of phosphate by the La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels.

Gel	C_{in} *(mg/l)*	$q_{e,exp.}$ *(mg/g)*	*Pseudo-2nd-order kinetic parameters*			*Non-linear regression*		
			k [g/(mg·min)]	R^2	$q_{e,cal}$ *(mg/g)*	$q_{e,cal}$ *(mg/g)*	R^2	*k [g/(mg·min)]*
La(III)-loaded SOW gel	20	11	7.08×10^{-3}	0.99	11.1	11.05	0.983	6.42×10^{-3}
	40	15	5.87×10^{-3}	0.99	15.3	14.89	0.969	5.03×10^{-3}
Ce(III)-loaded SOW gel	20	11	9.59×10^{-3}	0.99	11.0	10.97	0.983	8.15×10^{-3}
	40	15	5.68×10^{-4}	0.99	17.1	16.75	0.988	7.01×10^{-3}
Zr(IV)-loaded SOW gel	20	15	1.17×10^{-3}	0.99	15.3	15.00	0.986	1.102×10^{-3}
	100	47.5	2.44×10^{-4}	0.99	49.0	48.65	0.987	2.15×10^{-4}
	260	76.2	2.27×10^{-4}	0.99	78.1	75.19	0.970	2.47×10^{-4}

10.2. EFFECT OF pH ON THE ADSORPTION OF PHOSPHATE

The pH of the aqueous solution is an important variable, which influences the sorption of both anions and cations at the solid-liquid interface. The anion exchange capacity is strongly governed by the pH of the solution and by the surface chemistry of the solids [66]. The effects of equilibrium pH on phosphate adsorption by the La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels were shown in Fig. 10.2. In this work, a wide range of pH (1-14) was studied to know the effect of pH on phosphate removal from aqueous solutions. It is seen from this figure that the La(III)- and Ce(III)-loaded SOW gels exhibit similar behavior for the adsorption of phosphate. The % removal sharply increases with increasing pH at pH values between 5 and 7 and then tends to approach a maximum value, which is maintained until pH 10 where after it decreases with further increases in pH. In contrast, Zr(IV)-loaded SOW gel showed quantitative removal of phosphate from pH 1 to 9. For an initial concentration of 20 mg-P/l, the final concentration of phosphate after treatment at pH 3 was found to be much lower than the permissible discharge limit of 0.5-1.0 mg-P/l. This result is very much inspiring to the use of the prepared gel.

The results of the adsorption tests can be interpreted in terms of a ligand exchange mechanism between the phosphate species and water molecules and/or hydroxyl ions coordinated with the metal ion immobilized on the gel as shown in Scheme 10.1. Since the lanthanum, cerium and zirconium ions tend to be extensively polymerized and hydrolyzed even at very low concentration and they convert into $[Ln(H_2O)_n]^{3+}$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species [67], respectively, a lot of hydroxyl ions as well as water molecules are therefore available for ligand exchange with phosphate species. The ligand exchange reaction has been further confirmed by the fact that the pH has either increased or not quite changed after the adsorption of phosphate at various initial pH.

In aqueous environment, phosphate can exist in different ionic species such as monovalent $H_2PO_4^-$, divalent HPO_4^{2-}, and trivalent PO_4^{3-} ions, depending on the pH of the solution (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.33) [68]. At pH lower than 4, the dominant species is $H_2PO_4^-$ becomes protonated to H_3PO_4, which are considered to substitute neutral water molecule from the hydrated metal ions loaded onto the gel. These protonated neutral species are weakly favored for adsorption onto the La(III)-

and Ce(III)-loaded SOW gels, which eventually leads to low removal of phosphate from the solution at low pH. On the other hand, at pH values between 5 and 10 the predominant phosphate species are HPO_4^{2-} and $H_2PO_4^-$, which may be strongly adsorbed onto the La(III)- and Ce(III)-loaded SOW gels by electrostatic interaction. Neutral species of phosphate (H_3PO_4), however, can be adsorbed onto the Zr(IV)-loaded SOW gel at pH lower than 2 by substituting water molecules from the hydrolyzed zirconium coordination sphere. At pH between 2 and 9, the dominant species are $H_2PO_4^-$ and HPO_4^{2-}, which may also be more or less adsorbed onto the Zr(IV)-loaded SOW gel with the substitution of hydroxyl ligands of the loaded zirconium. This was further supported by the increase in solution pH after equilibration.

Figure 10.2 also shows that, for all adsorption gels, % removal of phosphate decreases with further increase in pH (at higher pH range), which can be attributed to the competition between hydroxyl ions and phosphate ions for adsorption sites.

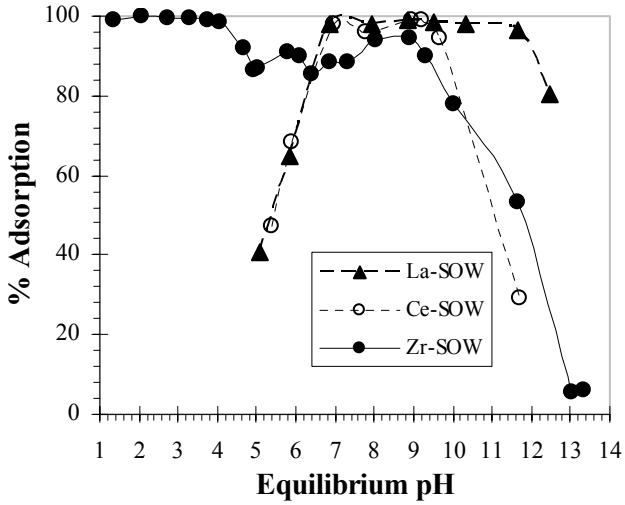
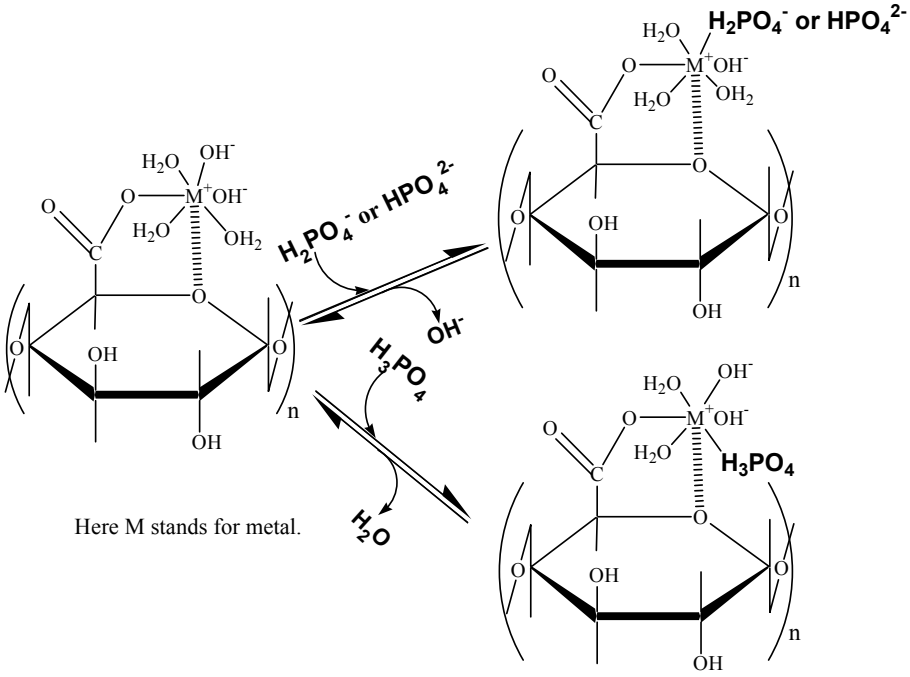


Fig. 10.2. Effect of pH on the adsorption of phosphate onto La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 20 mg/l, t = 24 h, T = 30°C.

However, different sorption behavior observed for the Zr(IV)-loaded SOW gel compared to that for the La(III)- and Ce(III)-loaded SOW gels may be explained by the physicochemical properties of the loaded metal ions. The extremely low value of the solubility product of $Zr(OH)_4$ compared to those of $La(OH)_3$ and $Ce(OH)_3$ may

have an effect on the adsorption of phosphate. Since lanthanides have coordination numbers of 6, 8, 9 [69] or even more, e.g. 10 or 11, which allow to take various geometries while zirconium has a coordination number of 4, 6, 8 [67], the differences in the coordination spheres may also be responsible for the different adsorption behavior between the Zr(IV)-loaded and lanthanides(III)-loaded SOW gel systems.



Scheme 10.1. Inferred mechanism for phosphate adsorption onto the metal-loaded SOW gels.

10.3. EFFECT OF OTHER COMPETING ANIONS ON THE ADSORPTION OF PHOSPHATE

Municipal and industrial wastewaters always contain sulfate and chloride anions which may compete with the target phosphate for the adsorption sites and hence the efficiency of the gel may reduce. To assess the competing effect of other anions on phosphate removal by the La(III)-loaded SOW gels, phosphate batch adsorption tests were carried out by equimolar (0.65 mM) addition of other anions such as sulfate, chloride, and carbonate as shown in Fig. 10.3, which signifies that such foreign anions have minimal interference in the adsorption of phosphate on the La(III)-loaded SOW gel.

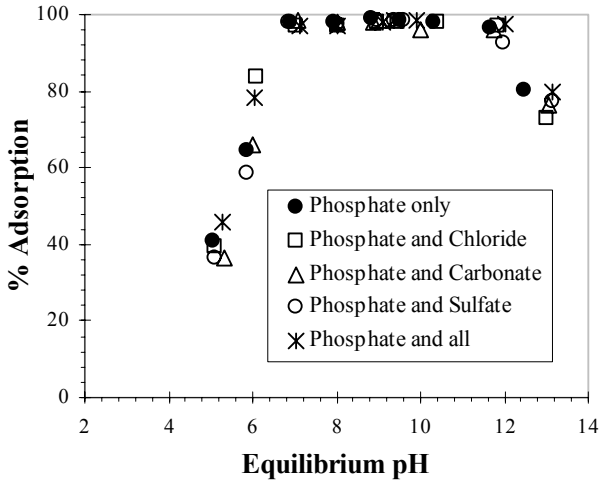


Fig. 10.3. Effect of other anions on phosphate removal using La(III)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

In the similar way, tests were performed in order to assess the competing effect of other anions on phosphate removal by the Zr(IV)-loaded SOW gel. Batch adsorption tests of phosphate (0.20 mM) were carried out by addition of other anions such as chloride (0.56 mM), carbonate (0.33 mM) and sulfate (0.42 mM) as shown in Fig. 10.4, which signifies that such foreign anions cause minimal interference with the adsorption of phosphate on the Zr(IV)-loaded SOW gel. Such observations can be attributed to the fact that the affinity between the gel and tested competing anions is weaker than that between the gel and phosphate.

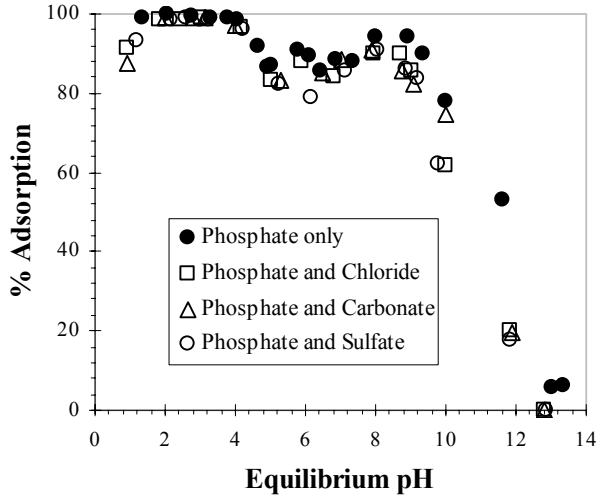


Fig. 10.4. Effect of other anions on phosphate removal using Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

The effect of presence of As(V) was also tested using the Zr(IV)-loaded SOW gels as shown in Fig. 10.5. This figure shows that As(V) can not interfere to the adsorption of phosphate from aqueous solution by using the Zr(IV)-loaded SOW gel. This is possibly due to the stronger affinity of phosphate ions towards adsorption sites.

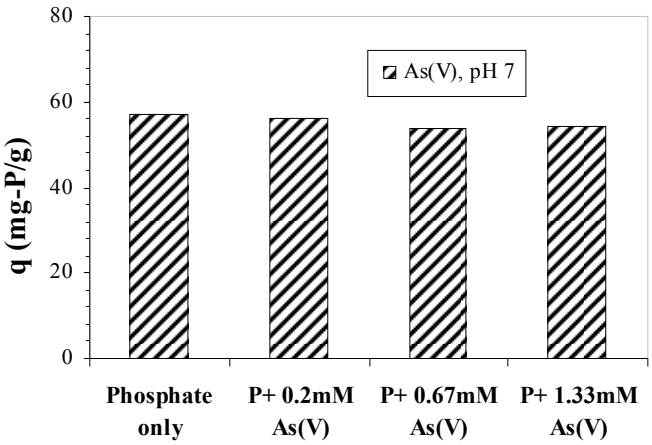


Fig. 10.5. Effect of presence of As(V) on phosphate removal using Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

10.4. ADSORPTION ISOTHERMS

Static sorption capacity gives the idea to what extent the functional sorption can be achieved. In this work the La(III)-, Ce(III)- and Zr(IV)-loaded SOW gels were tested to find their sorption capacity for phosphate adsorption. Fig. 10.6 shows the phosphate adsorption isotherms for the La(III)- and Ce(III)-loaded SOW gels at pH 7.5 for both gels. Fig. 10.7, on the other hand, shows the same for the Zr(IV)-loaded SOW gel, Zr(IV)-loaded MUROMAC and zirconium ferrite at pH 7 for all gels. However, Zr(IV)-loaded MUROMAC and zirconium ferrite are commercially available adsorbents and have been used in this study to compare the adsorption capacity. As seen from Fig. 10.6 and 10.7, the adsorption increases with increasing concentration of phosphate at low phosphate concentrations, and tends to approach constant values at higher concentration, suggesting that it is adsorbed onto these adsorbents according to the Langmuir adsorption mechanism for each adsorbent tested. From the constant values at the plateau region (Fig. 10.6 and 10.7), the maximum phosphate adsorption capacity was evaluated as 13.94 mg-P/g for both the

La(III)- and Ce(III)-loaded gels while sorption capacities for the Zr(IV)-loaded SOW gel, the Zr(IV)-loaded MUROMAC and zirconium ferrite were 57, 13 and 43 mg-P/g, respectively. The considerable high value of sorption capacity for Zr(IV)-loaded SOW gel suggests that the modification of orange waste by loading with Zr(IV) is justifiable in terms of the enhanced phosphate adsorption. However, phosphate adsorption capacity of Zr(IV)-loaded SOW gel at pH 3 was also tested and found to be 105 mg/g. This is possibly due to the fact that the maximum adsorption (%) of phosphate occurs at pH 3 (Fig. 10.2). A comparison of phosphate adsorption capacities of various adsorbents (Table 10.2) indicates that the gels used in the present study has much higher capacity, which leads a stride towards its application.

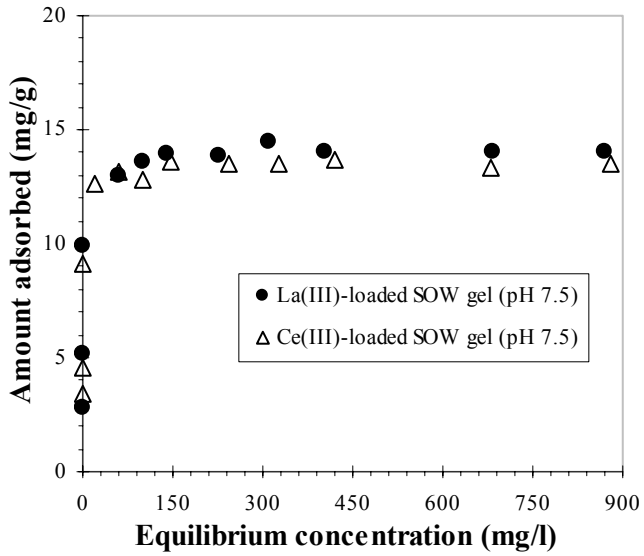


Fig. 10.6. Adsorption isotherms for phosphate on La(III)- and Ce(III)-loaded SOW gels. Conditions: S/L ratio = 1.67 mg/ml (for both gels), t = 24 h, T = 30ºC.

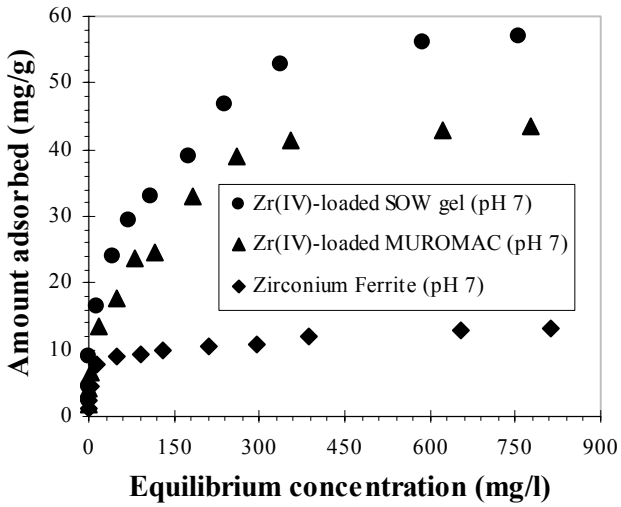


Fig. 10.7. Adsorption isotherms for phosphate on different adsorbents. Conditions: S/L ratio = 1.67 mg/ml (for Zr(IV)-loaded SOW gel and Zr(IV)-loaded MUROMAC), 3.33 mg/ml (for zirconium ferrite), t = 24 h, T = 30ºC.

Table 10.2. Comparison of maximum sorption capacity with other adsorbents.

Adsorbent	q (mg-P/g)	pH	Reference
La(III)-loaded orange waste	13.9	7.5	Present study
Ce(III)-loaded orange waste	13.9	7.5	Present study
Zr(IV)-loaded orange waste	57	7	Present study
	105	3	Present study
$ZnCl_2$ activated coir pith	5.1	4	[26]
Iron oxide tailings	7	6.6-6.8	[70]
MgMn-layered double hydroxide	7.3	-	[71]
Aluminum oxide hydroxide	0.37-0.76	-	[72]
Synthetic goethite and akaganeite	10	7.7	[73]
Wood fiber	4.3	-	[74]
Goethite	2.79	3.5	[75]

10.5. EFFECT OF TEMPERATURE AND STUDY OF THERMODYNAMIC PARAMETERS

The variation of sorption with temperature was studied from 30°C to 60°C (303 to 333 K) for the Zr(IV)-loaded SOW gel under the optimized conditions. The removal

of phosphate was found to be slightly increased with the increase in temperature as shown in Fig 10.8. The increase in adsorption of phosphate with temperature might have been due to dissolution of the adsorbing species and/or enlargement of the pore size, which eventually help to enhance the rate of intra-particle diffusion [76-78]. The data obtained at 303, 313, 323 and 333 K were fitted well with pseudo-second-order kinetics. According to the Arrhenius equation (Eq. 9), a relationship between natural logarithm of rate constant (k) and inverse of temperature (T) was plotted in Fig. 10.9, from where the activation energy (E_a) was calculated to be 44.91 kJ/mol. It is to be noted here that T is the temperature (K) and A and R the pre-exponential factor and universal gas constant (kJ/mol), respectively.

$$k = Ae^{-E_a/RT} \tag{9}$$

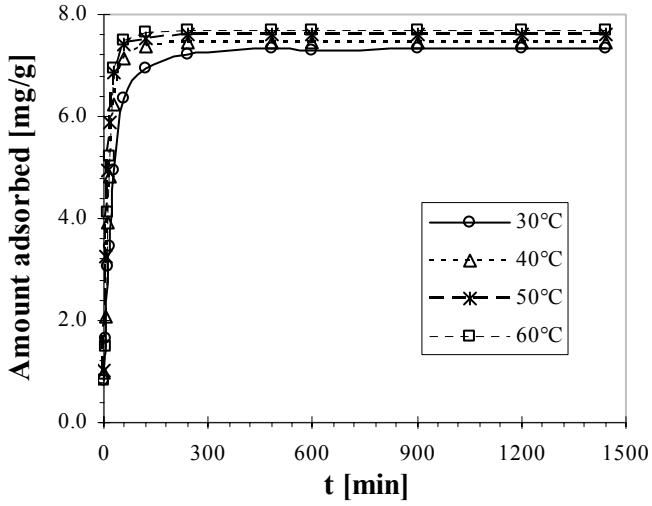


Fig. 10.8. Time dependence of phosphate adsorption onto Zr(IV)-loaded SOW gel at different temperature.

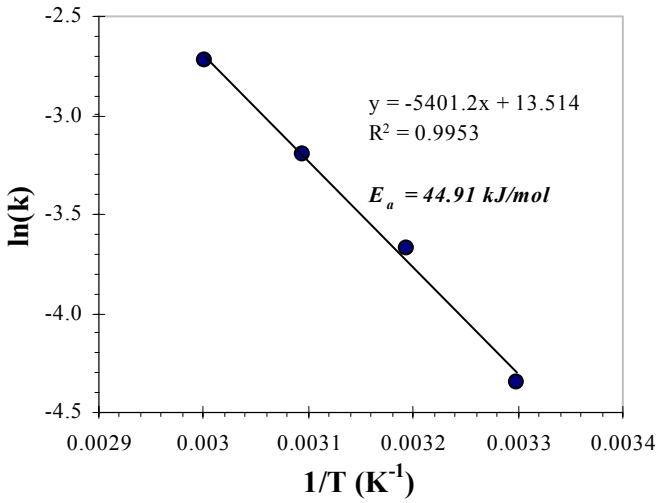


Fig. 10.9. Variation of sorption of phosphate onto Zr(IV)-loaded SOW gel with temperature.

The thermodynamic parameters for the adsorption systems were calculated using the following equations [79] and the values are given in Table 10.3:

$$K_d = \frac{C_{ad}}{C_{eq}} = \frac{a}{1-a} \tag{10}$$

$$\Delta G^0 = -RT\ln(K_d) \tag{11}$$

$$\Delta H^0 = E_a - RT \tag{12}$$

$$\Delta S = \Delta H^0 - T\Delta S^0 \tag{13}$$

where K_d is the equilibrium constant, C_{ad} the adsorbed amount of phosphate at equilibrium, a the uptake of phosphate at equilibrium, $\Delta G°$ the change in Gibbs free energy (kJ/mol), $\Delta S°$ the change in entropy (kJ/(mol·K)) and $\Delta H°$ the change in enthalpy (kJ/mol). The positive value of $\Delta H°$ suggests the endothermic nature of adsorption and in addition to that, the extent of the change in enthalpy indicates that the adsorption type is chemisorption. However, the values of $\Delta G°$ become more negative with increasing temperature, which indicates the spontaneity of the process. The positive value of $\Delta S°$ shows the increased randomness at the solid/solution interface during the adsorption of phosphate on the gel.

Table 10.3. Thermodynamic parameters for the adsorption of phosphate on Zr(IV)-loaded SOW gel.

C_{in} (ppm)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(mol·K))	$\Delta G°$ (kJ/mol)		
			303 K	313 K	323 K
12.5	42.2	0.17	-12.05	-13.1	-14.4

10.6. DYNAMIC ADSORPTION AND ELUTION TESTS

The performance of the La(III)- and Zr(IV)-loaded SOW gels in continuous operation for the removal of phosphate was studied using a packed column as described in Section 4.8. Figure 10.10 shows the breakthrough profiles of phosphate with the La(III)-loaded SOW gel at pH 7 and the Zr(IV)-loaded SOW gel at pH 3 and 7, which were individually carried out and where the feed concentration for every event was maintained at around 20 mg-P/l. Figure 10.10 illustrates that the breakthrough occurred at 140 and 60 BV for the La(III)-loaded SOW gel (at pH 7) and the Zr(IV)-loaded SOW gel (at pH 7), respectively, while the complete saturation of the bed was achieved correspondingly at 320 and 815 BV. The effective or dynamic adsorption capacities of these gels were calculated to be 13.63 and 10 mg-P/g, which were low compared to that of the Zr(IV)-loaded SOW gel operated at pH 3. It is to be noted that, the dynamic adsorption capacity for the Zr(IV)-loaded SOW gel at pH 3 was found to be 36 mg-P/g. The higher adsorption capacity at low pH can be attributable to the strong adsorption behavior of the Zr(IV)-loaded SOW gel at pH 3 as demonstrated earlier in Fig. 10.2. Such study shows that the orange waste gel loaded with Zr(IV) can be used for phosphate removal in continuous-mode very effectively at pH 3. However, the dynamic adsorption capacity of zirconium ferrite, a commercial resin, was also tested at neutral pH and found to be very low (2.6 mg-P/g) compared to that of the metal-loaded SOW gel. From such comparison, it can be concluded that the orange waste gel can be better utilized for wastewater treatment.

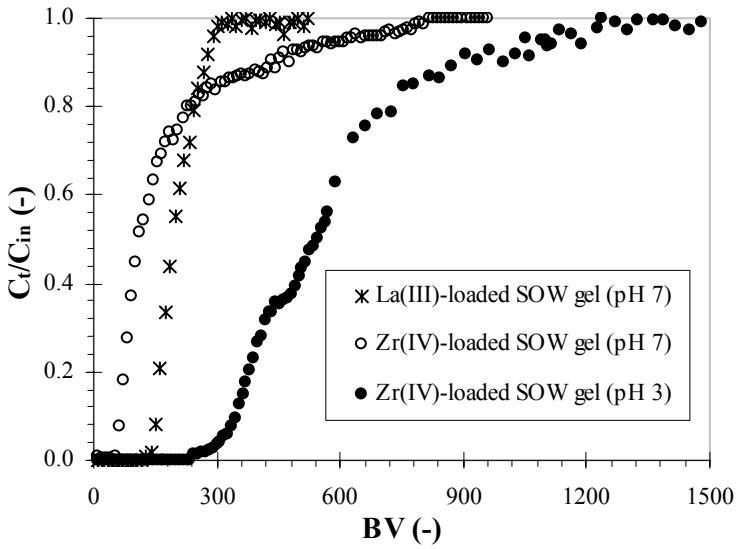


Fig. 10.10. Column adsorption tests for phosphate using (*) La(III)-loaded SOW gel (flow rate = 7 ml/h), (•) Zr(IV)-loaded SOW gel (flow rate = 5 ml/h) and (○)Zr(IV)-loaded SOW gel (flow rate = 5.7 ml/h). Here C_t and C_{in} denote the adsorbate concentration in the effluent at time t and the initial concentration.

When the column undergoes complete saturation, elution tests were carried out by using either HCl or NaOH. Typical elution curves for phosphate using the different metal-loaded SOW gels are depicted in Fig. 10.11, which shows that nearly 20 fold and 10 folds preconcentration of phosphate have been occurred respectively for the Zr(IV)-loaded SOW gel and the La(III)-loaded SOW gel, which were previously operated at neutral pH for adsorption. Approximately 85% of the adsorbed phosphate was eluted from the bed of the La(III)-loaded SOW gel by using a small amount of 0.4 M HCl. However, the problem with this system is that the loaded lanthanum was also eluted along with phosphate during the operation. So it is necessary to load lanthanum before carrying out the next operation. On the other hand, quantitative recovery (more than 95%) of the preconcentrated phosphate was found to be occurred from the Zr(IV)-loaded SOW gel by using 0.2 M NaOH. In case of column packed with the Zr(IV)-loaded SOW gel and operated at neutral pH shows more than 40 folds preconcentration of phosphorus. Furthermore, no zirconium was leaked during the elution process which ensures regeneration of the column only by water washing.

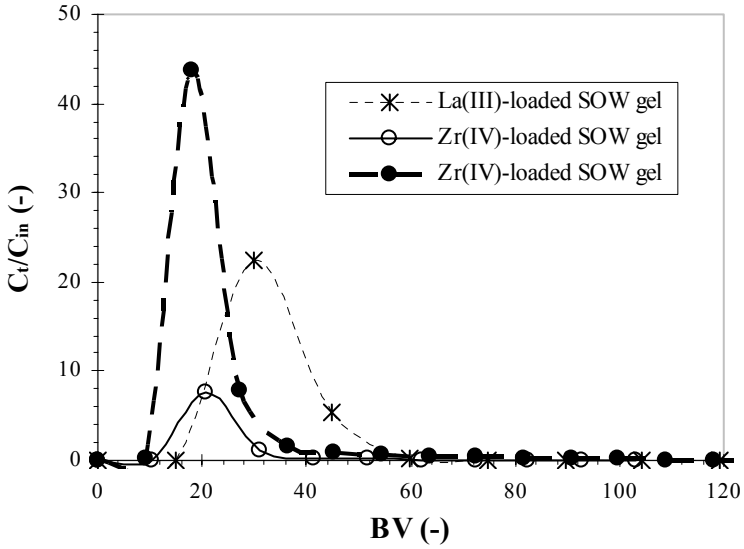


Fig. 10.11. Column elution tests for phosphate using (*) La(III)-loaded SOW gel (flow rate = 9 ml/h), (•) Zr(IV)-loaded SOW gel (flow rate = 5 ml/h) and (○) Zr(IV)-loaded SOW gel (flow rate = 5.7 ml/h).

10.7. APPLICATION OF Zr(IV)-LOADED SOW GEL

The Zr(IV)-loaded SOW gel has been tested for its application in industrial wastewater treatment in the view of phosphate removal. At the same time, a prospective application has been figured out in the treatment of spent electroless nickel plating solution. Finally, the gel has been tested to recover phosphorus from the leach liquor, which has been obtained after leaching of IASA.

10.7.1. Treatment of industrial effluent and reutilization of gel

In connection to the repeated use of the Zr(IV)-loaded SOW gel, cycle tests were carried out by using real effluent from the facility of the biological treatment by activated sludge provided by Saga Prefectural Livestock Experiment Station, Saga, Japan. The effluent sample was used as received (pH 3.24 and concentration 38 mg-P/g). This experiment was carried out up to 9 cycles and a good extent of adsorption as well as elution was achieved as shown in Fig. 10.12.

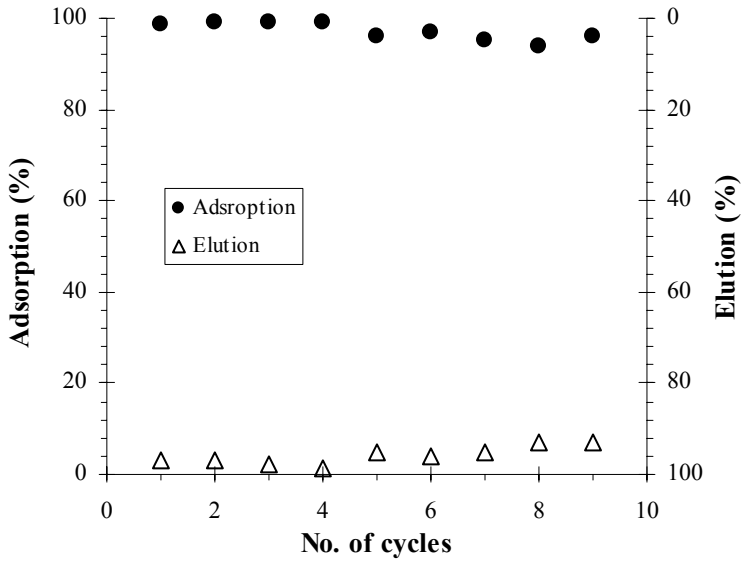


Fig. 10.12. Adsorption-elution profile of phosphate onto Zr(IV)-loaded SOW gel. Conditions: C_{in} = 38 mg-P/l, eluting reagent = 0.2 M NaOH.

10.7.2. Prospective application in treating spent electroless nickel-plating solution

Nickel coating on an objective via electroless nickel plating is produced by controlled chemical reduction of nickel ions on a suitably treated surface. Many important physical properties such as uniformity, corrosion resistance, and hardness are better than those of electroplated nickel [80]. These advantages have made electoless nickel plating an attractive process from product finishing. However, sodium hypophosphite is by far the most common reducing agent because of the lower cost, greater ease of control and better overall plating quality relative to most other reducing agents. The reducing ability of such agent decreases after repeated uses, and finally becomes unusable. Thus hundreds of thousands of waste containing phosphorus species go to the environment, which ultimately affect the biodiversity.

Tests using the Zr(IV)-loaded SOW gel was carried out in the view of separating phosphite, hypophosphite and phosphate. Figure 10.13 shows the % removal with respect to pH where it is seen that all these three phosphorus species could be adsorbed in acidic region. Although quantitative adsorption of phosphate occurred up to pH 9.5, the maximum adsorption for phosphite and hypophosphite took place at pH 4 and pH 3.5, respectively. Considering the speciation of phosphate [44] and

phosphite [81], it is evident that monovalent and divalent phosphate species ($H_2PO_4^-$, HPO_4^{2-}) as well as phosphite species ($H_2PO_3^-$, HPO_3^{2-}) are responsible for such adsorption, while only monovalent hypophosphite [81] ion ($H_2PO_2^-$) is responsible to take part into this adsorption process. Fig. 10.13 indicates that there is the possibility of mutual separation among phosphate, phosphite and hypophosphite between pH 4.5 to 9 because at any pH value in the mentioned range, the removal of these three species differs from each other. So a careful adjustment of pH of the mixed solution would help to separate the wanted species from others.

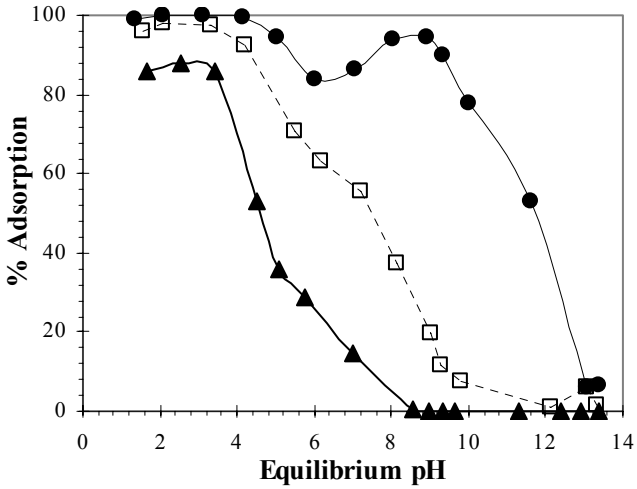


Fig. 10.13. Effect of pH on the adsorption of (●) phosphate, (□) phosphite and (▲) hypophosphite onto Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 20 mg/l (for each), T = 30°C, t = 24 h.

Figure 10.14 shows the sorption isotherms of phosphate, phosphite and hypophosphite onto Zr(IV)-loaded SOW gel operated at their optimum pH values which are 3, 2 and 2.5, respectively. From Fig. 10.14 the maximum sorption capacities of phosphate, phosphite and hypophosphite were calculated to be 105, 148 and 50 mg/g, respectively. The enhanced phosphate adsorption capacity of the gel signifies its application to the wastewater treatment in lieu of conventional processes, while the high adsorption capacity of phosphite and hypophosphite can be of interest in electoless nickel plating to recover those reducing agents from spent solution.

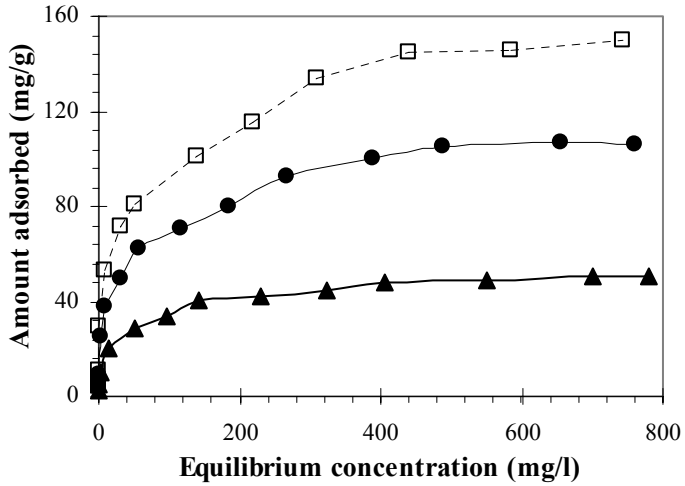


Fig. 10.14. Adsorption isotherms for (●) phosphate, (□) phosphite and (▲) hypophosphite onto Zr(IV)-loaded SOW gel. Conditions: S/L ratio = 1.67 mg/ml, t = 24 h, T = 30ºC.

10.7.3. Recovery of phosphorus from leach liquors

Incinerated activated sludge ash (IASA) is a phosphorus-rich residue, which can be chemically treated to recover phosphorus from it. In this work an attempt was made to first extract phosphorus from IASA and then recover it from the leachate by means of adsorption using the Zr(IV)-loaded SOW gel.

The IASA, collected from Kumamoto Nambu Sewage Treatment Center, Japan, was undergone total dissolution with concentrated acids (aqua regia, sulfuric acid, hydrochloric acid and nitric acid) at boiling temperature. The insoluble residue was double baked until totally dissolved. The solutions were then diluted and the containing elements were measured by using a Shimadzu model ICPS-8100 inductively coupled plasma-atomic emission spectrometer (ICP/AES). Thus the elemental compositions were obtained as shown in Table 10.4, which summarizes that the sample contains phosphorus, calcium, aluminum, iron as major elements irrespective of the kind of dissoluting reagents. Apart form these elements, there are magnesium, manganese, copper and zinc are present. However, cadmium and lead was not found in the incinerated activated sludge ash. From the viewpoint of rich phosphorus content, the IASA appeared to be an attractive resource if phosphorus could be recovered.

Table 10.4. Elemental composition (mg/g) of IASA.

Elements	Dissoluting reagents			
	Aqua regia	H_2SO_4	HCl	HNO_3
P	87.956	67.943	81.345	82.975
Ca	56.533	58.936	53.869	56.353
Al	60.356	33.015	34.703	41.615
Fe	52.084	17.919	46.760	11.293
Mg	19.263	11.839	15.841	16.136
Mn	1.222	0.748	1.101	1.036
Cu	0.715	0.498	0.569	0.508
Zn	---	0.447	1.027	0.583
Pb, Cd	0	0	0	0

The IASA was undergone leaching with H_2SO_4, HCl and NaOH at different conditions by varying the parameters such as liquid/solid ratio, concentration, temperature and time. However, H_2SO_4 and HCl were found to be effective in extracting phosphorus while NaOH was not so efficient (Fig. 10.15). Through several experiments 0.05 M H_2SO_4 at 150 ml/g and 0.05 M HCl at 250 ml/g were found to be the optimum conditions for leaching IASA, which were eventually used for further leaching tests.

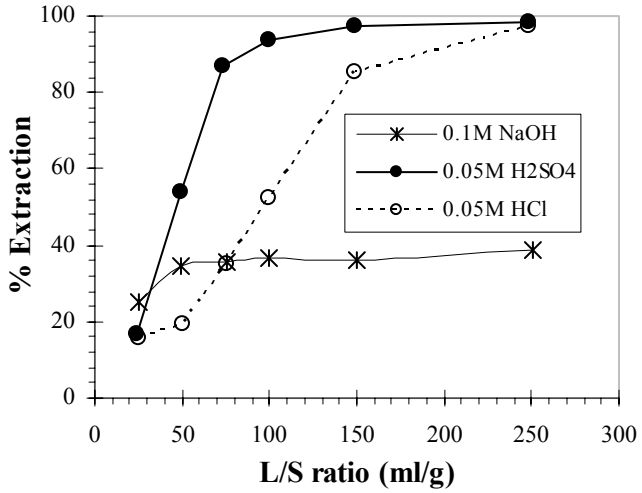


Fig. 10.15. Extraction of phosphorus from IASA by using different chemicals. Conditions: shaking time = 7 h (for acids) and 24 h (for NaOH), T = 30ºC.

After complete extraction of the elements from IASA by using above mentioned acids, the challenge remains in selective recovery of phosphorus from the leachate. The pH of the leachate was between 1.7 and 1.89. Since the pH of the leachate is low, the Zr(IV)-loaded SOW gel was used to adsorb phosphate because it can uptake phosphorus at lower region of pH. Figure 10.16 shows that the Zr(IV)-loaded SOW gel can effectively adsorb phosphate from both the leach liquor solutions at and above of 10 mg/ml. The other elements (Al, Fe, Ca, Mn, Mg, Cu etc.) present in the solution did not interfere to the adsorption process. At the same time, none of these metal ions was found to be adsorbed onto the gel. This can be attributed to the fact that the binding sites of the gel for cation exchange are already occupied by Zr(IV).

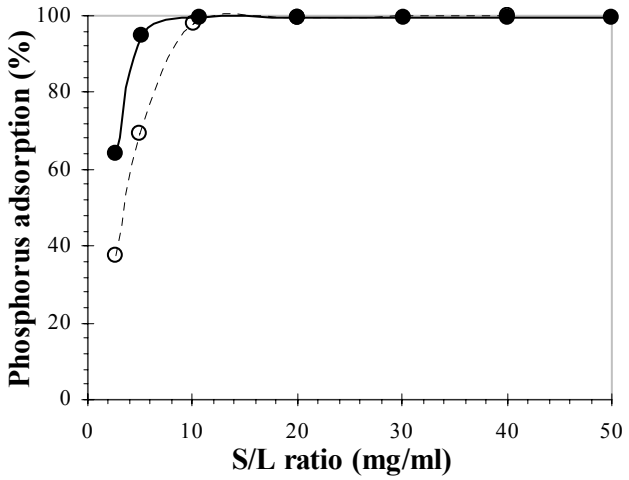


Fig. 10.16. Adsorption of phosphorus onto Zr(IV)-loaded SOW gel from leach liquor of IASA. Legends: (•) 0.05 M HCl leachate, (○) 0.05 M H_2SO_4 leachate. Conditions: t = 24 h, T = 30ºC.

So from such tests, it can be seen that the Zr(IV)-loaded SOW gel can be used to recover the important element (phosphorus) from IASA. Thus a sustainable treatment of phosphorus resource, in the form of IASA, has been opened up in order to its recovery.

Chapter 11

Conclusion

The pH is shown to be one of the key variables for phosphate removal. In this connection, maximum phosphate removal occurs at around neutral pH for all gels. Equilibrium adsorption data for phosphate was in good agreement with Langmuir isotherms, from which the maximum sorption capacity was evaluated. The adsorption of phosphate was found not to be influenced by the addition of other anions such as chloride, carbonate, sulfate and arsenate. The Zr(IV)-loaded SOW gel was found to be effective not only for synthetic solution but also for real solution. Considerably high adsorption capacity and its repeated use for adsorption have pointed towards widespread application of this gel. Column adsorption followed by elution studies using a fixed bed suggests that the metal-loaded SOW gels can be used in a continuous-mode operation to remove phosphate from wastewater and other industrial effluents contaminated with phosphate. It also shows that phosphate can be easily eluted by using either HCl or NaOH solution after preconcentration of phosphate ions on the gel. Such elution experiments are the indicative measure of recovery of phosphate.

The attempt to recover phosphate from IASA was also successful. The extraction of phosphorus from the IASA was found to occur with acids. The phosphorus was successfully recovered from the leachate by using the Zr(IV)-loaded SOW gel.

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Chapter 12

Overall conclusion and future directives

Part I and II give brief conclusions, which include comments and summary of the specific themes investigated relevant to each part. The overall concluding remarks of this dissertation, the unsolved analysis for this investigation and the future direction of concerned issues are highlighted in this chapter.

12.1. OVERALL CONCLUSION

Even though the application of conventional removal methods for arsenic and phosphorus are widespread in various industries but they have some drawbacks: selection of optimum dosing of chemicals and at the same time sludge production and handling in coagulation-filtration method, lack of selectivity in presence of competing anions and high price of commercial resins in ion exchange method, requirement of power in filtration method etc. are few to mention. Thus a need to develop an efficient, cheap and environmentally benign adsorption gel was felt for the effective removal of arsenic and phosphorus from contaminated aqueous medium.

In connection to that, increased demand of processed citrus fruits in market drove business personalities to produce citrus juice which generates high amount of wastes. Orange waste is one such precursor which can be abundantly obtained from the orange juice factories. Low price and availability of orange waste as well as its potentiality to adsorb anions has made it a good choice for preparing adsorbent by using it. With an objective of removal and recovery of arsenic and phosphorus, orange waste, a cheap and available agricultural by-product, has been treated by a simple chemical modification where after it has been further loaded with the La(III), Ce(III) and Zr(IV) to obtain three different adsorption gels. Orange waste consists of pectin molecules, cellulose, hemicellulose and so forth. It was first chemically modified by tailoring the methylated ester part of pectin molecules and then loaded with the mentioned metal ions. The chemical modification was simple and done by washing with $Ca(OH)_2$, which has been termed as saponification. However, the metal ions

were immobilized/loaded onto the saponified orange waste (SOW) and adsorption behavior of all gels for arsenic and phosphate were studied.

Sorption capacity for arsenate as well as arsenite was tested and found to be superior to other adsorbents reported in literature. Adsorption of arsenate was found to be unaffected with the presence of other competing anions such as chloride, carbonate and sulfate. Phosphate, on the other hand, causes reduction in arsenate adsorption from the aqueous solution. The dynamic adsorption capacity of La(III)- and Zr(IV)-loaded SOW gel were also tested and found to be effective for carrying out adsorption tests in continuous-mode. In addition to that, the Zr(IV)-loaded SOW gel was tested for up to six adsorption-elution cycles for As(V) in column-mode. The amount of arsenate adsorbed onto the gel packed in column and eluted from the column verified that As(V) could be quantitatively recovered under the tested condition.

The prepared gels were tested to remove phosphate from contaminated solution too. Sorption capacity for phosphate uptake was compared with that of two commercially available resins namely zirconium ferrite and MUROMAC XMC 3614. The Zr(IV)-loaded SOW gel was found to be superior to those commercial resins from the viewpoint of adsorption capacity. Moreover, the gel did not show any interference of other competing anions (e.g. chloride, sulfate, carbonate, arsenate etc.) during phosphate adsorption onto it. Column adsorption and elution tests indicated the practical use of the gel. However, a waste solution containing phosphorus was collected from Saga Prefectural Livestock Experiment Station, Saga, Japan and tested to remove phosphorus from that solution. The results were encouraging since the Zr(IV)-loaded SOW gel was found to be effective for phosphate removal up to 9 adsorption-elution cycles. In addition phosphorus was extracted from IASA and Zr(IV)-loaded SOW gel was employed to recover the element from the leachate.

Since the preparation method for the gel is quite simple, which requires less chemicals, the production cost is presumed to be low if the production plant is constructed and operated in the vicinity of orange juicing factories. Taking into account of the gels' efficiency, cost and benign behavior towards environment, the prepared gels could be considered as alternatives to conventional resins and adsorbents to separate hazardous anions from water and wastewater. However, since

the present adsorption gel is prepared from orange waste, a bio-material, it will be difficult to use for a long time with many repeats of adsorption followed by elution contrary to plastic resins. After elongated use of the gel, it will be degraded, for example, by the attack of microorganisms. In such cases, the loaded metal can be easily recovered by interacting with strong acid and can be used for reloading again on fresh gel to prepare the metal-loaded SOW gel while degraded unloaded orange waste gel can be safely treated without any trouble e.g. by incineration or by composing to make fertilizer.

Hence in summary, a novel use of an agricultural by-product (orange waste), which is environmentally benign and biodegradable, has been found that can contribute to the environmental protection and to reduce human sufferings caused by the presence of hazardous anions in aquatic environment. Moreover, recycling and recovery of a limiting nutrient, phosphorus, has also been found to be come about in nice fashion.

12.2. DIRECTION FOR FUTURE WORK

In this science era, faster growing technology promotes mankind to enhance their standard-of-living. The prerequisite for this technological development is the research and development in the sector of science and technology. Even though the research and development are an endless task, human beings are eagerly looking for the future for the latest invention so that it can help protecting the balance of nature. In this context, the research work delineated in this dissertation may serve as a primary foundation for the welfare of human kind and conservations of the nature which will interestingly lead to future study. A few directions of future work are depicted here which exclude the fundamental accomplishments of the present study.

12.2.1. Analytical task

Apart from the experimental work there are some analytical jobs too that have to be performed for better understanding of sorption mechanism. The loading of metal ions onto the orange waste gel is a complex phenomenon which includes the physicochemical properties of loaded metal, force of attraction between adsorbent and adsorbate, formation of inner and outer coordination spheres in aqueous medium. So

analysis of all such things may help to comprehend the sorption mechanism much better.

12.2.2. Upgradation of column facilities

Even though the used experimental setup was well designed and the data obtained from this setup was reliable and of good accuracy the unwanted encroachment of air bubble in the column at times may be avoided by designing it sophisticatedly.

12.2.3. Use of carrier

Since the prepared gel is a degradable fine particle and the sustainability at high pressure has not been tested, the direct utilization of such gel in industry may not be fitted well. Therefore to make it robust, a carrier, which should be inert in nature, may be employed on which the gel can be pasted. However, in this case it has to be ensured that the active sites of the gel have not been covered so much.

List of publications:

1. **Biplob Kumar Biswas**, Katsutoshi Inoue, Kedar Nath Ghimire, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, Removal and recovery of phosphorus from water by means of adsorption onto orange waste gel loaded with zirconium. Bioresource Technology, doi:10.1016/j.biortech.2008.04.015

2. **Biplob Kumar Biswas**, Katsutoshi Inoue, Kedar Nath Ghimire, Hidetaka Kawakita, Keisuke Ohto, Hiroyuki Harada, Effective removal of arsenic with lanthanum(III)- and cerium(III)-loaded orange waste gels, Separation Science and Technology, 43 (2008) 2144-2165.

3. **Biplob Kumar Biswas**, Jun-ichi Inoue, Katsutoshi Inoue, Kedar Nath Ghimire, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel, Journal of Hazardous Materials, 154 (2008) 1066-1074.

4. **Biplob Kumar Biswas**, Katsutoshi Inoue, Kedar Nath Ghimire, Shingo Ohta, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, The adsorption of phosphate from an aquatic environment using metal-loaded orange waste, Journal of Colloid and Interface Science, 312 (2007) 214-223.

5. **Biplob Kumar Biswas**, Kedar Nath Ghimire, Katsutoshi Inoue, Keisuke Ohto, Hidetaka Kawakita, Adsorptive separation of arsenic and phosphorus from an aquatic environment using metal-loaded orange waste, Journal of Ion Exchange, 18 (2007) 428-433.

Appendix B

Contribution to scientific forums:

1. Biplob Kumar Biswas, Katsutoshi Inoue, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, Adsorptive removal of phosphate, phosphite and hypophosphite from aqueous solution using Zr(IV)-loaded orange waste. *39th autumn meeting of Society of Chemical Engineers Japan*, 13-15 September 2007, Hokkaido University, Japan.

2. Biplob Kumar Biswas, Kedar Nath Ghimire, Katsutoshi Inoue, Keisuke Ohto, Hidetaka Kawakita, Adsorptive separation of arsenic and phosphorus from an aquatic environment using metal-loaded orange waste. *4th International conference on ion exchange*, 15-19 October 2007, Chiba University, Japan.

3. Biplob Kumar Biswas, Jun-ichi Inoue, Katsutoshi Inoue, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, Use of orange waste and pectic acid gel for arsenic removal. *5th International conference on Interfaces Against Pollution*, 1-4 July 2008, Kyoto University, Kyoto, Japan.

Appendix C

Curriculum Vitae of

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M.Sc. in Quality, Safety and Environment
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B.Sc. in Chemical Engineering
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November 1990
Higher Secondary Certificate (H.S.C.)
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July 1988
Secondary School Certificate (S.S.C.)
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Record of Employment:

2000-
Deputy Manager
Bangladesh Oil, Gas and Mineral Corporation (Petrobangla)
Dhaka, Bangladesh.

1999-2000
Assistant Engineer
Khulna Newsprint Mills Ltd.
Khulna, Bangladesh.

1997-1999
Assistant Engineer
Gas Transmission Company Limited
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Professional membership:
Society of Chemical Engineers Japan (SCEJ)
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Computing:
Proficient in MS Office package
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Basic knowledge of FORTRAN and MATLAB

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English (fluent)
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